A Fundamental Study on Refining of Titanium and Its Aluminides

Toru H. Okabe

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Preface

The present thesis is a summary of the author's studies on refining of titanium and its alloys, which have been carried out during April, 1988 ~ June, 1992 under the supervision of Professor Katsutoshi Ono, Department of Metallurgy, Kyoto University, in Japan.

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Introduction

Part I Introduction

Titanium and its alloys have been essential to the aerospace industry since the early fifties, because they combine high strength to weight ratio with the ability to perform at much higher temperatures than aluminum or magnesium alloys. They also have growing usage in the chemical processing industries because of its excellent resistance to chloride corrosion.

A majority of metallic titanium is made by the "Kroll process"[1][2] which involves the chlorination of the concentrate with a subsequent reduction of tetra–chloride by electrolytically produced metallic magnesium in a inert gas atmosphere. The product of the "Kroll process" is a metallic sponge which is later consolidated by a high temperature arc melting. The most important consideration for any process of titanium production is to prevent contamination either metallic or non–metallic impurities, because even small amount of oxygen or nitrogen can make the product brittle and unworkable, although carefully controlled amount of oxygen, nitrogen and carbon may be added to strengthen titanium alloys.

The level of purity of the commercial grade Kroll titanium sponge is between 99 and 99.99% in total metallic impurities (excluding gaseous elements) with the major impurity being oxygen at several hundred mass ppm(about 0.05%) even in the purest sponge.

In the view of the very pronounced affinity of titanium metal for oxygen and nitrogen, it is necessary to start with oxygen–free and nitrogen–free titanium compounds, preferably titanium tetrachloride, in titanium refining process. Also due to its reactiveness, titanium refining and melting process has to be carefully isolated from air and ceramics. There is no suitable crucible for melting other than water cooled copper crucible, because titanium in liquid state is extremely reactive and easy to be contaminated at high temperatures. The reaction to produce titanium metal is, therefore, operated at relatively low temperatures about 1200K in a gas tight stainless steel reaction vessel. This batch type process, which produce solid state titanium sponge, is difficult to modify to continuous process, and is expensive, thus raising the price of the final product, which prevents it from being more widely used in industry.

Several efforts to develop the new process for titanium production[3]–[5], such as direct electrowinning of titanium from its chloride of oxide using molten salt, were made, whereas there is no process which is competitive to the Kroll process today. Development of new refining process is essential to reduce production cost which minimizes its usage in a potentially widespread market.

At this stage removal of oxygen accumulated in titanium scrap is the most substantial factor for titanium recycling, because oxygen contamination is unavoidable during processing of titanium products such as heat treatment. As effective method for direct deoxidation of titanium has not yet developed currently, highly oxygen contaminated titanium is diluted by low oxygen content titanium sponge, and recycled. Therefore, development of effective titanium recycling process is also very important.

For the age titanium is commonly used, it is obvious that a fundamental study on refining titanium and its alloys is of greatest significance. The author is one of the researchers who dedicated his doctor course life for this fundamental study.

a. History of Refining of Titanium

Titanium element was isolated in the year 1790 and named after the Titans of mythology in 1795[6]. This element was found to exist in iron sand as oxides, whereas metallic titanium could not extracted as for its strong affinity with oxygen, nitrogen and carbon. As the years went on some interests appeared in the literature but more than a century was to pass before the metal was isolated in massive form and another half century elapsed before the full realization of the process of metal production.

Study on refining of metallic titanium was carried out by Nilson and Petterson[2][7] in late 19th century, who reduced titanium tetrachloride by sodium metal, and recognized the sensitivity of titanium to gases. Similar attempt to produce metallic titanium using sodium metal was done by many researchers in the early twentieth century, but ductile titanium metal was hardly obtained.

In 1910, Hunter[8] reduced titanium tetrachloride to ductile metal by use of sodium metal in a steel bomb. This research was carried out with the scope of exploring new ductile refractory metal for use of a filament in lamp. There was feverish activity directed towards replacing carbon filament with a high melting metal filament these days [6]. No pure titanium had been produced up to that time, and the melting point of titanium was reputed to be of the order of 6000K, therefore, result of melting point measurements of the Hunter titanium caused great disappointment of Hunter, and glamour attached to titanium metal as a filament material disappeared.

While the Hunter process for production of ductile sponge titanium using sodium metal was first demonstrated in 1910, its introduction on a commercial scale did not occur until 1955[9][10].

In 1925, Van Arkel and de Boer[11][12] precipitated small amount of highly pure titanium on a hot tungsten filament by utilizing dissociation of titanium iodide gas by a disproportionation reaction. This method, so called iodide process, has been applied for the further purification of titanium[13] because the purity of titanium was much better than titanium produced by the metallothermic reduction processes. Characterization of pure titanium was made by using this "iodide titanium"[12].

In 1940, Kroll proposed a new method to produce ductile titanium by reducing tetrachloride in an argon atmosphere using magnesium metal[2]. The first production of titanium sponge commercially available was reported in 1946 by the U.S. Bureau of Mines where 15–lb batches of good quality sponge were made by the Kroll process. In 1947, 1t sponge titanium by this Kroll process was commercially produced by Dupont Corporation in the United States[3].

Classical methods to obtain metallic titanium by reducing $TiCl_4$ using an electrolytically produced alkaline metal or metallic magnesium are high energy consumption, and also are inefficient batch type processes. The iodide process is suitable process for producing high purity titanium, however the reaction speed is very low and is impractical for mass-productive commercial application. These processes referred to above are expensive, while electrowinning of titanium directly from titanium tetrachloride has an advantage of low cost, because this process needs no metallic reducing agent so that it needs lower overall energy consumption[14]. That is, electrowinning of titanium seems to have an excellent industrial potential for the commercial production of titanium metal, if some operational problems can be solved.

Development of principles of electrowinning processes using molten salt electrolysis was taking place concurrently with the evolution of the thermochemical process of titanium reduction. A broad study of the electrochemistry of titanium had been started in the 1940's, with the object of selecting a new process for winning metallic titanium[15]. In Japan, Tomonari[5], Hashimoto[16], Watanabe[17] started extensive investigation on electrowinning and electrorefining of titanium in the 1960's.

Study on fused salt electrolysis of titanium has principally concerned oxides as source electrolytes, but attempts to electrolytically reduce TiO_2 and other oxides to metal in alkali chloride melts have met with failure to produce high purity titanium[15][18][19]. Existing literature on titanium halide electrolysis, as a second process, concerns fluorides and chlorides exclusively, with only casual reference to bromides and iodides. This process was in reality a chemical reduction or an indirect electrolysis to produce ductile titanium, and, therefore, both intensive and extensive invesitigation was carried out. A third general type of electrolytic procedure proposed for titanium is soluble anode fusion electrolysis[20][21]. Such a procedure would have its primary application as a refining operation where off–grade titanium would be employed as an anode in a titanium bearing melt and deposited in purified form at the cathode[22]. According as the extensive investigation of titanium refining, thermodynamic properties of titanium and its halide and oxides in molten salts were studied[23][24], and to date, electrochemical study on titanium in molten salt was conducted by many researchers[25]–[27]. In most cases, oxygen or carbon species in molten salt turned out to deteriorate the purity of titanium deposits.

Literature on electrolytic cells for the production of titanium from molten salt is quite extensive. Although some of the associated works have been developed at pilot plant scale with the aim of the electrolytic production of metals in industrial plants, the lack of specifically designed hardware, did not permit the full exploitation of the processes at that time. Important examples of this state of affairs are provided by the activities of the U.S. Bureau of Mines[28][29], and of companies like New Jersey Zinc[30], TMCA[31], Cezus[32], D–H Titanium[33], Albany Titanium[37], and more recently, Ginatta[34]–[35]. Almost all of these methods utilizes halide salt electrolytic procedures with several similarities. In most cases $TiCl_4$ or K_2TiF_6 is the starting material and dendritic titanium deposits were obtained from the molten salts kept at temperatures between 700 and 1200K.

In Japan, Tokumoto *et al.* developed a new process to produce flat and smooth titanium plate directly from a fused electrolyte[38][39][40]. Dendritic or powdery deposition of titanium on cathode is one of the serious drawback of titanium electrolysis, therefore, their efforts were meaningful and outstanding but the process was too complicated to apply for commercial applications.

High temperature reaction, called Halomet process[41], which produces liquid titanium from titanium chloride gas by magnesium reduction was also investigated intensively with the scope of developing an effective continuous titanium production process, but no successful results were obtained.

In the recent years, Japanese titanium producers cooperated to investigate a new continuous titanium refining method. This method utilizes continuous gas phase reaction between titanium chloride and magnesium vapor to produce solid titanium particles continuously[42]. No substantial results have been reported at this stage.

A process which can take place the Kroll process has not emerged, but continuous efforts for research on refining of titanium will result in evolution of an effective process which leads titanium being more widely used in industry.

b. Metallothermic Reduction and Deoxidation

In 1937, Kroll has reported on the reduction of TiO_2 by pure Ca that ductile titanium is not obtainable simply by direct reduction of its oxides with usual reducing agent such as magnesium or calcium[1]. Marden employed this calciothermic reduction of oxide to produce vanadium and thorium metal, and improved upon it very decidedly by adding salts, especially $CaCl_2$ to the mixture of oxide and calcium in a reaction bomb[2][43][44]. Kroll also employed this process on a larger scale using readily fusible $CaCl_2$ and $BaCl_2$ additions. By this modified Marden process, 98% pure titanium was obtained but the product after melting was brittle due to the presence of oxygen[2].

In 1950's Lilliendahl[45] [46] applied metallic calcium for deoxidation of zirconium metal, and obtained zirconium metal containing 200 mass ppm oxygen[47][45]. In 1958, Rostron[48] claimed a patent for direct thermal reduction of titanium dioxide by using metallic magnesium at a temperature substantially not less than 1273K with a subsequent deoxidation by calcium metal. In this patent, he showed possibility that [48] calcium could be dispersed in a fused calcium chloride bath maintained at about 1300K or higher, and could be used to deoxidize titanium metal.

In spite of these many efforts, previous workers have concluded that the conventional metallothermic deoxidation methods are not suitable for direct removal of oxygen dissolved in titanium [2], because these days all attempts to produce low–oxygen titanium by the calciothermic deoxidation were failed. This unsuccessful result can be attributed to misunderstanding in the knowledge of oxygen affinity with titanium and calcium. Thermodynamic properties of oxygen in dilute titanium–oxygen alloy was not clearly investigated at this time, and calcium thought to be incapable of complete reduction of Ti–O alloys[15]. Trial to produce low–oxygen titanium was discontinued, because it was known that iodide process could produce high purity titanium containing about 100 mass ppm oxygen.

In the recent years, some new processes to produce titanium were investigated from the standpoint of developing costly favorable process. Paixao[49] claimed in his patent a process for obtaining metallic titanium from an anatase (TiO_2) concentrate by an aluminothermic or magnesium–thermic reaction. More recently, Maeda's research group also demonstrated aluminothermic reduction of titanium oxide with a subsequent electron beam melting of the obtained titanium–aluminum alloy for aluminum and oxygen removal[50]. By this process titanium containing about 0.06% oxygen was produced.

As an another approach to overcome the high cost for the production of titanium ingot, extensive research was carried out in developing several near net shape technologies such as powder metallurgy, because parts made by the powder metallurgy offer mechanical properties equal to or superior to parts made from ingots.

In 1984, Ono started systematic study on calciothermic reduction of titanium oxide with the scope of producing fine titanium powders[51][52]. This investigation was extended to the direct synthesis of fine titanium aluminide powders directly from oxides[53], utilizing knowledge of reduction diffusion techniques, which is developed for producing rare–earth alloy powders for use in magnets[54]–[11]. The similar process to produce titanium–alloy powders by calcium was investigated by Herget[3] in the same year.

The development of an effective process for deoxidation of titanium could find application in the recovery of titanium scraps and in the production of low oxygen–containing titanium powders[59]. Recently, RMI company, which quitted production of titanium sponge by the Hunter process, started new process for recycling titanium scraps using calciothermic deoxidation process[60]–[62]. The process named DOSS process, an acronym for DeOxidation in the Solid State process, is directed to the deoxidation of titanium turnings which contain oxygen in relatively small amounts as surface or interstitial impurities. In this process, titanium powders which contain less than about 1 percent oxygen are deoxidized by calcium in a Ca–Na liquid alloy, and produced titanium containing several hundred mass ppm oxygen.

Since 1950's it has been thought that oxygen removal directly from titanium is impossible to the level below 100 ppm by the conventional metallothermic deoxidation. From a thermodynamic view point, external gettering used for solid state refining is turned out to be one of the most promising methods for direct deoxidation of titanium[63][64]. Oxygen removal directly from titanium using this method was investigated by the author with the purpose of producing high purity titanium below 50 mass ppm oxygen. This oxygen level is now the technical limit attainable by the conventional processes, i.e. iodide process and electrorefining process.

c. High Purity Titanium

Over the past several years, the demand for high purity titanium for use in electronic materials has increased[65]. For applications such as target materials for semiconductor use, 99.99 to 99.999% (excluding gaseous elements) high purity Kroll titanium has been mainly employed. More recently, for electronic materials use, titanium is purified further by using method of the iodide process[66][67] or electrolytic refining[68][69]. The level of purity of titanium produced in these ways is between 99.999 and 99.9999% (excluding gaseous elements), with the major impurity of 99.9999% titanium being oxygen at about 100 mass ppm. As the presence of oxygen in titanium leads to deterioration of titanium thin films[70], it seems important to produce low oxygen titanium for semiconductor use.

Among the known purification processes (e.g. electrolysis in molten salts, electron beam floating zone melting, electro–transport, and degassing in ultra high vacuum), no effective methods other than electrolytic refining and iodide refining have been developed for oxygen removal to a level below 100 mass ppm. Even if low oxygen titanium is successfully produced using these optimized methods, contamination by oxygen is inevitable during subsequent processing, such as during electron beam melting.

The iodide process produces titanium with total metallic impurities being less than 10 mass ppm whereas major impurity is oxygen at a level between 50 and 150 mass ppm level. As this process utilizes thermal decomposition of titanium iodide gas, the rate of production is very small and process controls are difficult. In recent years, Yoshimura, at Osaka Titanium Co. Ltd,. developed this process on a large scale to produce high purity titanium for electronic material[67].

A process for electrorefining of titanium was pioneered in the 1950's and 1960's at the US Bureau of Mines station in Boulder City Nevada[69]. ElectrolyticΩ titanium was produced on the research scale until 1985 when the ALTA Group in the United State started producing high purity elecrorefined titanium on a commercial scale. Nishimura *et al.*, at Nippon Mining Co. Ltd, also succeeded in producing electrolytically refined titanium which contain less than 1 mass ppm in total metallic impurities and 80 mass ppm oxygen[71].

d. Thermodynamics of Titanium–Oxygen Solid Solution

It is well known that a large amount of oxygen dissolves in titanium to form an interstitial solid solution. The maximum solubility of oxygen in hexagonal close–packed titanium (α–Ti) is about 33 mol%. The oxygen solubility in the high temperature bcc phase (β–phase) is much lower (about 2 mol% at 1273K) and the α–β transformation temperature increases sharply with increasing oxygen content.

As mentioned above, oxygen removal directly from titanium–oxygen solid solution to a level below 100 mass ppm level has been deemed to be difficult because titanium has a strong affinity for oxygen. In any discussion of the feasibility of preparation of extra–low–oxygen titanium, knowledge of oxygen activity in titanium, in other words, the partial molar free energy of oxygen,$\Delta\overline{G}_O$, in β–titanium is needed.

Oxygen activity measurements in β–titanium solid solution are, however, not easy because of the extremely low oxygen partial pressure in titanium–oxygen solid solution[72]. This low value of oxygen partial pressure makes it difficult to use conventional methods to measure $\Delta\overline{G}_O$. Some thermodynamic investigations have been made by using an indirect method to determine the activity of oxygen in β–titanium[52][73][74], but these values are not consistent with each other.

Among the previous studies concerning thermodynamic properties of dilute titanium–oxygen solid solution, Kubaschewski and Dench[73] firstly measured the concentration of oxygen around 1273K for three compositions of Ti–O solid solution by equilibrating titanium with magnesium, calcium, barium and their respective oxides. They adopted an equilibrium oxygen concentration in titanium, for example, under Ca–CaO co–existence, which was the lowest value of various analytical results ranging from 0.07 to 0.24 mass%.

Mah *et al.*[75] measured the heats of formation and the heat capacities of Ti–O alloys up to 1600K. They found that the partial molar enthalpy of oxygen at 298K does not vary significantly with oxygen content up to 25 mol% oxygen. Combining these values, they determined $\Delta\overline{G}_O$ for the α field with the aid of a simple model to estimate configurational entropy. By extrapolating $\Delta\overline{G}_O$ which was deduced from their data for α–solid solution and with various assumptions, they estimated $\Delta\overline{G}_O$ for the β field. Their estimation includes a large amount of uncertainty because they had to use the data of α/β phase boundaries as well as the partial molar heat capacity of oxygen in α–solution.

The method employed by Kubaschewski has been extended by Komarek and Silver[76]. They determined $\Delta\overline{G}_O$ for the α–titanium solution in the temperature range between 1073 and 1273K. $\Delta\overline{H}_O$ and $\Delta\overline{S}_O$ were deduced by differentiating $\Delta\overline{G}_O$.

Based on hydrogen partial pressure measurements in the ternary Ti–O–H system at 1073K, the activities of oxygen in the binary Ti–O system were estimated up to 14 mol% oxygen by Hepworth and Schuhmann[77]. They concluded that hydrogen stabilizes β–phase and increases oxygen activity coefficient.

Boureau and Gerdanian[78] applied the microcalorimetric method to determine $\Delta\overline{H}_O$ at 1323K in titanium–oxygen solid solution. $\Delta\overline{S}_O$ in the α and β solutions and $\Delta\overline{G}_O$ within β field were also computed. Tetot *et al.*[79] improved the experimental apparatus and re–measured $\Delta\overline{H}_O$ with high precision.

Ono and Miyazaki[52] modified the method employed by Kubaschewski and Dench[73] to measure the deoxidation limit of titanium by calcium and magnesium at temperatures between 1173K and 1573K. By using measured oxygen contents, they estimated the thermodynamic properties of oxygen in β–Ti–O solid solutions. Recently, Sano and Tsukihashi[74] used the same method and obtained activities of oxygen in β–titanium in the temperature range 1373–1573K by using their original value of the standard free energy of formation of CaO[80]. The equilibrium oxygen concentration in titanium obtained recently by Sano and Tsukihashi[74][81] differs significantly from that obtained by Ono and Miyazaki at high temperatures[52].

e. Survey of This Thesis on Refining of Titanium and Its Aluminides

With the background mentioned above, and also with the scope of developing new process for refining titanium, the author has carried out the following studies to clarify the thermodynamic properties of oxygen in dilute titanium–oxygen solid solution, and discussed feasibility of producing extra–low–oxygen titanium. Using this knowledge, the author developed some processes for direct reduction and deoxidation of titanium. Characterization of the products were also carried out by trace element analysis, electrical resistivity and micro Vickers hardness measurements. These studies on refining of titanium were compiled in Part II.

Not only several findings in Part II but also thermodynamic consideration of the Ti–Al–Ca system were applied for refining of titanium aluminide powders. The author developed effective methods for direct reduction of titanium aluminide powders from mixtures of both oxides. The results and discussions of reduction and deoxidation of titanium aluminides were complied in Part III.

e.1 Part II : Refining of Titanium

Thermodynamic properties of dilute titanium–oxygen solid solution in β field was investigated in chapter 1. Oxygen activities of titanium in beta phase were determined by equilibrating titanium–oxygen alloys with calcium and CaO at temperatures between 1173 and 1473K. The method chosen in this study is that first used by Kubaschewski and Dench[73]. Thermodynamic properties of oxygen in the solid Ti–O alloys were discussed by using the data obtained in this study and the standard free energy of formation of CaO. This knowledge was applied to discuss the feasibility of preparation of extra–low oxygen titanium.

The advanced deoxidation method were examined in chapter 2 to attain the lower oxygen level according to the thermodynamic viewpoint. An experimental investigation directed towards the preparation of extra–low–oxygen high purity titanium by using the calcium halide flux deoxidation method were carried out with the purpose of producing highest purity titanium. Several factors in choosing fluxes and the process parameters for deoxidation were considered, and feasibility to produce extra–low–oxygen titanium was discussed. Titanium wires and small pieces were deoxidized to the level below 100 mass ppm by calcium–halide flux deoxidation technique at around 1273K.

In chapter 3, the electrolytically refined high purity titanium produced by Nishimura *et al.*[71] was further deoxidized to the level below 20 mass ppm oxygen. Characterization of extra–low–oxygen titanium was carried out using this deoxidized high purity titanium. Trace element analysis, micro Vickers hardness measurements, and electrical resistivity measurements were carried out.

As an alternate method for deoxidation, electrochemical deoxidation of titanium was examined in chapter 4 with the purpose of obtaining oxygen–free–titanium. Removal of oxygen in titanium using an electrochemical technique was examined at temperatures around 1223K, and oxygen concentration in titanium was lowered to below the detection limit of conventional inert gas fusion analysis.

In chapter 5, some attempts for direct reduction of titanium oxides by calcium or calcium hydride were made. Fine titanium powders containing several mass ppm oxygen were produced by the calciothermic reduction of oxides.

e.2 Part III : Refining of Titanium Aluminides

Mechanical properties of TiAl have been intensively investigated in the recent years, and consolidated parts made of the titanium aluminide powders by hot isostatic press have been turned out to be very useful. The author has carried out the following studies with the scope of developing effective process to produce clean and fine titanium aluminide powders, because there has been considerable interest in developing titanium aluminides as a structural material.

The direct compound reduction techniques, called the co–reduction or reduction–diffusion(RD) process, was investigated with the purpose of producing low oxygen titanium aluminide powders directly from oxides, because plasticity of TiAl has proven to be influenced by impurities such as oxygen[82]. Oxygen removal directly from TiAl to a level below 100 mass ppm is deemed to be very difficult, therefore, one of the effective deoxidation methods developed in the previous part was applied for refining of titanium aluminide powders with the purpose of producing extra–low–oxygen titanium aluminide.

Prior to the calciothermic reduction and deoxidation investigation, thermodynamic study on phase equilibria in the Ti–Al–Ca system at the reaction temperatures were investigated in chapter 1 to determine the composition of Ca–Al alloys in equilibrium with titanium aluminide. Phase equilibria in the Ti–Al–Ca–O system were evaluated on the base of the recent thermodynamic data and the experimental results obtained in this study.

Using the knowledge of phase relation and experience acquired from the study in Part II, the composition of the Ca–Al alloy deoxidant and experimental conditions suitable for the preparation of extra–low–oxygen TiAl was decided. TiAl powders were deoxidized to several tens mass ppm at around 1373K under controlled aluminum activity.

In chapter 3, study on preparation of TiAl and Ti_3Al powders by calciothermic reduction of oxides was carried out at 1273K. Several reducing agents and feed materials were tested to optimize the reducing conditions, and clean and fine compound powders were produced.

A fundamental study on preparation of $TiAl_3$ powders by calciothermic reduction of oxides were also carried out in chapter 4.

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Part II

Refining of Titanium

Chapter 1

Thermodynamic Properties of Dilute Titanium–Oxygen Solid Solution in Beta Field

1.1 Introduction

It is well known that a large amount of oxygen dissolves in titanium to form an interstitial solid solution, as shown in Figure 1.1 [1]. The maximum solubility of oxygen in hexagonal close-packed titanium (α–Ti) is about 33 mol%. The oxygen solubility in the high temperature bcc phase (β–phase) is much lower (about 2 mol% at 1273K) and the $\alpha - \beta$ transformation temperature increases sharply with increasing oxygen content.

Oxygen removal directly from titanium–oxygen solid solution to a level below 100 mass ppm level has been deemed to be difficult because titanium has a strong affinity for oxygen. In any discussion of the feasibility of preparing extra–low oxygen titanium, knowledge of the partial molar free energy of oxygen, $\Delta\overline{G}_O$, in β–titanium is needed.

Oxygen activity measurements in β–titanium solid solution are, however, not easy because of the extremely low oxygen partial pressure in titanium–oxygen solid solution[2]. This low value of oxygen partial pressure makes it difficult to use conventional methods to measure $\Delta\overline{G}_O$. A few thermodynamic investigations have been made by using indirect methods to determine the activity of oxygen in β–titanium [3, 4], but these values are not consistent with each other.

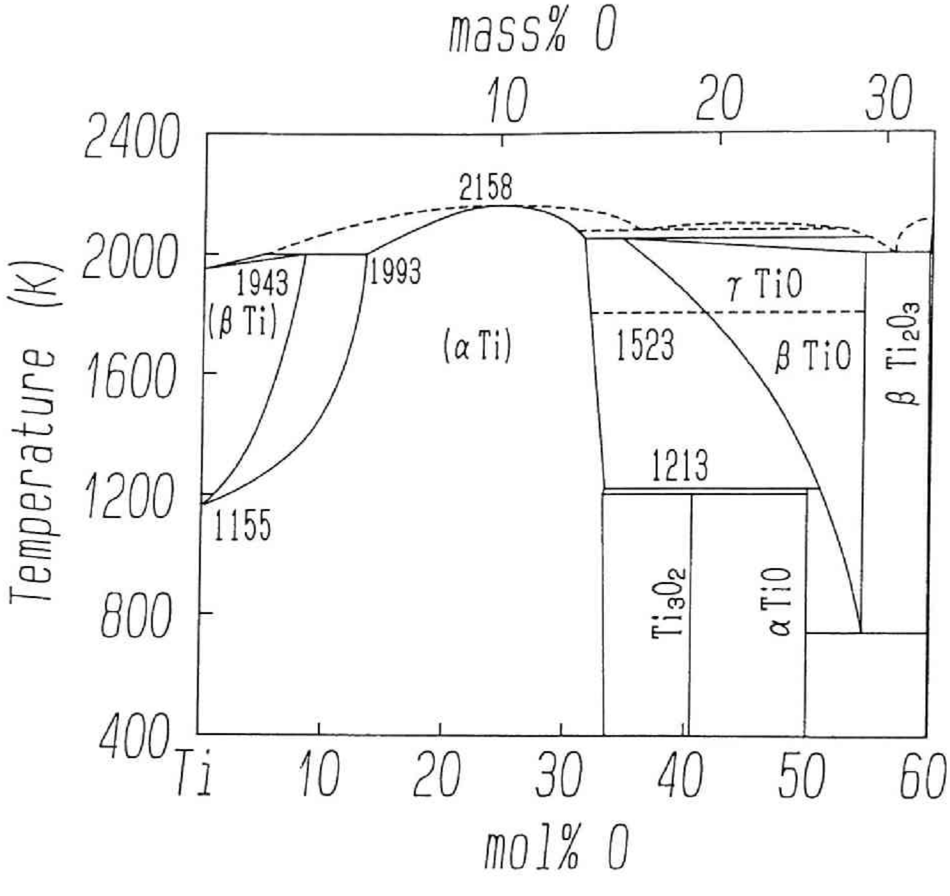

Figure 1.1: Phase diagram of the Ti–O system [1].

In this study, the partial pressure of oxygen in β–titanium solid solution was determined by use of calcium–calcium oxide equilibrium with the purpose of discussing the feasibility of deoxidation of titanium a level below 100 mass ppm. The method chosen in this study is that first used by Kubaschewski and Dench[5]. Titanium samples were allowed to react at a given temperature with an excess amount of mixture of calcium metal and its oxide until equilibrium was reached. The reaction can be written;

$$\mathrm{Ca\ (l\ or\ g)} + [\mathrm{O}]\ \mathrm{in\ Ti} = \mathrm{CaO\ (s)} \tag{1.1}$$

The solubility of calcium in titanium is reported to be very small, about 60 mass ppm at 1273K[4], so that the Ti–O alloys in equilibrium with calcium and calcium oxides may be represented by the Ti–O binary system. Thermodynamic properties of oxygen in the solid Ti–O alloys were discussed by using the standard free energy of formation of CaO.

1.1.1 Previous studies

Kubaschewski and Dench[5] measured oxygen concentrations in Ti–O solid solution around 1273K for three compositions by equilibrating titanium with magnesium, calcium, barium and their respective oxides. Figure 1.2 schematically indicates relationship between oxygen partial pressure and oxygen concentration in titanium at 1273K determined by Kubaschewski and Dench[5]. The analytical oxygen concentrations in titanium under Ca–CaO co-existence were ranging from 0.07 to 0.24 mass%, therefore, they adopted the lowest value as an equilibrium value among the obtained values.

Mah *et al.*[7] measured the heats of formation and the heat capacities of Ti–O alloys up to 1600K. They found that the partial molar enthalpy of oxygen at 298K does not vary significantly with oxygen content up to 25 mol% oxygen. Combining these values, they determined $\Delta\overline{G}_O$ for the α field with the aid of a simple model to estimate configurational entropy. By extrapolating $\Delta\overline{G}_O$ which was deduced from their data for α–solid solution and with various assumptions, they estimated $\Delta\overline{G}_O$ for the β field. Their estimation includes a large amount of uncertainty because they had to use the data of α/β phase boundaries as well as the partial molar heat capacity of oxygen in α–solution.

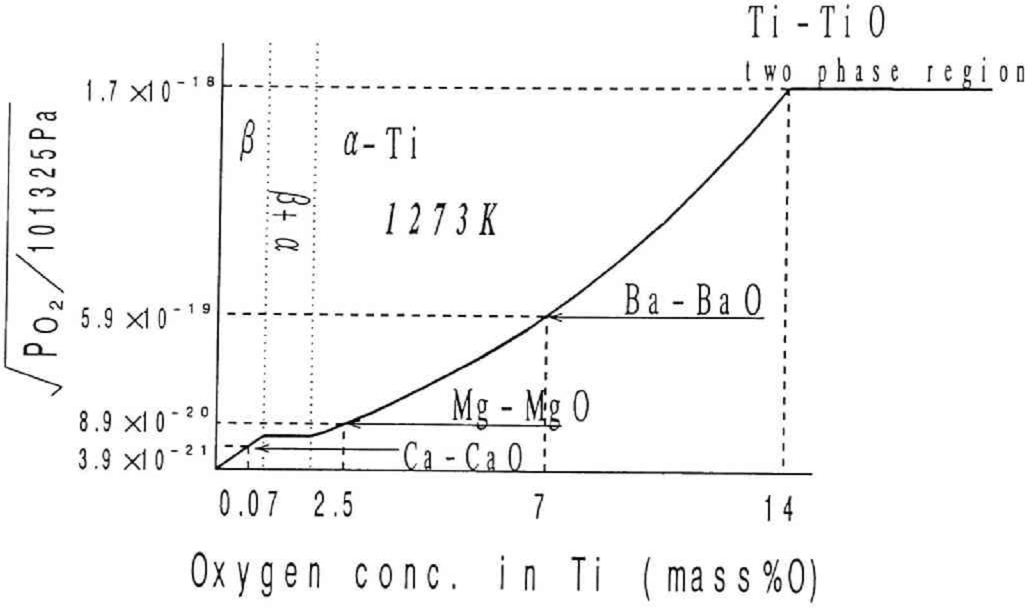

Figure 1.2: Relationship between oxygen partial pressure and oxygen concentration in titanium at 1273K determined by Kubaschewski and Dench[5].

The method employed by Kubaschewski and Dench[5] has been extended by Komarek and Silver[8] who determined $\Delta\overline{G}_O$ for the α–titanium solution in the temperature range between 1073 and 1273K. $\Delta\overline{H}_O$ and $\Delta\overline{S}_O$ were deduced by differentiating $\Delta\overline{G}_O$.

Based on hydrogen partial pressure measurements in the ternary Ti–O–H system at 1073K, the activities of oxygen in the binary Ti–O system were estimated up to 14 mol% oxygen by Hepworth and Schuhmann[9].

Boureau and Gerdanian[10] applied the microcalorimetric method to determine $\Delta\overline{H}_O$ at 1323K in titanium–oxygen solid solution. $\Delta\overline{S}_O$ in the α and β solutions and $\Delta\overline{G}_O$ within β field were also calculated. Tetot *et al.*[11] improved the experimental apparatus and re-measured $\Delta\overline{H}_O$ with high precision.

Ono and Miyazaki[3] modified the method employed by Kubaschewski and Dench[5] to measure the deoxidation limit of titanium by calcium and magnesium at temperatures between 1173K and 1573K. By using measured oxygen contents, they estimated the thermodynamic properties of oxygen in Ti–O alloys. Recently, Sano and Tsukihashi[4] used the same method and obtained activities of oxygen in β–titanium in the temperature range 1373–1573K by using their original value of the standard free energy of formation of CaO[12]. The equilibrium oxygen concentration in titanium obtained by Sano and Tsukihashi[4] differs significantly from that obtained by Ono and Miyazaki[3].

1.2 Experimental

1.2.1 Experimental procedures

Titanium samples were placed in a stainless steel container with calcium and CaO as shown in Figure 1.3. Several kinds of titanium samples produced by Kroll process with different initial oxygen concentrations were used as starting materials. Samples containing lower and higher oxygen contents than the equilibrium amount were used as starting materials so as to reach equilibrium from both sides.

Ten to fifteen pieces of titanium sample (about 0.1–0.5g each) were placed on a titanium dish within a titanium cup, which was filled with calcium and CaO. The cup containing the sample and calcium was set in the stainless steel container. Special

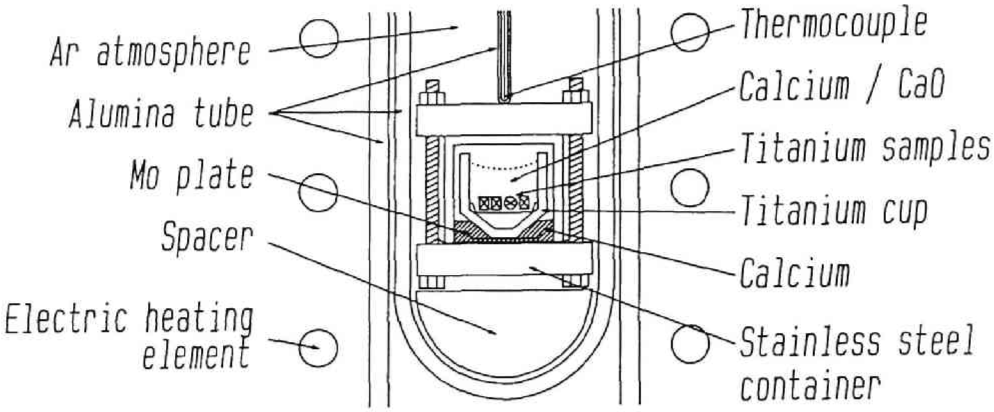

Figure 1.3: Schematic illustration of the experimental apparatus.

care was taken to avoid contamination from the container and the atmosphere (*e.g.* additional calcium nodules were placed in the space between the titanium cup and the container as a seal to prevent leakage from the container with the liquid calcium when the container was heated to the experimental temperature.)

The assembled container was heated in the furnace to a temperature between 1173 and 1373K, and the duration of the experimental was between 86.4ks and 260ks. The time necessary to reach equilibrium was evaluated by using oxygen diffusivity in titanium[13] and the solid state diffusion model[14], and was confirmed by oxygen analysis. The reaction container was then quenched in water. Calcium metal and CaO were removed by leaching with (1+1) acetic acid, and the resulting samples were carefully cleaned in warm HCl aqueous solution, rinsed with water, alcohol and acetone, and then dried.

Oxygen and nitrogen analyses of the samples were made using the inert gas fusion infrared absorption method (LECO TC–336 analyzer). For oxygen extraction, 0.1g of titanium sample enclosed in a 1g nickel basket was dropped into a graphite crucible and held above 2300K. The instrument was calibrated by using 1980 mass ppm oxygen titanium standard samples, and the measured values were cross checked by analyzing different titanium standard samples (440 and 1430 mass ppm). Calcium was chemically analyzed by the flame–less atomic absorption spectrometry.

1.3 Results

1.3.1 Oxygen concentration in titanium solid solution

Table 1.1 shows the analytical results for the oxygen concentration in titanium in equilibrium with calcium and CaO. The oxygen concentrations were essentially independent of specimen configuration and of the direction from which equilibrium was approached. The results confirm that the reaction time employed in this study was enough to reach equilibrium.

The results in Table 1.1 are plotted in Figure 1.4 together with the reported data [3]–[5]. The results of this work are in good agreement with the data reported most recently by Sano and Tsukihashi[4]. The data reported by Ono and Miyazaki[3] are the mean values of highly scattered results at a given temperature. Their data

Table 1.1: Analytical values of oxygen and nitrogen concentrations in titanium. Various types of titanium samples with different initial oxygen concentrations were equilibrated with calcium and CaO.

Exp. No.	Reaction temperature (K)	Reaction time (ks)	Oxygen conc. (mass ppm)		Nitrogen conc. (mass ppm)
			Initial	After equilibrium	After equilibrium
Eq-1	1173	260	200	310	430
			720	300	1090
Eq-2	1223	173	200	430	840
			450	380	630
			720	400	1430
Eq-3	1273	86	430	460	340
			1430	470	470
Eq-4	1323	86	200	600	880
			720	580	1760
			1200	590	990
Eq-5	1373	86	200	760	260
			1200	760	540

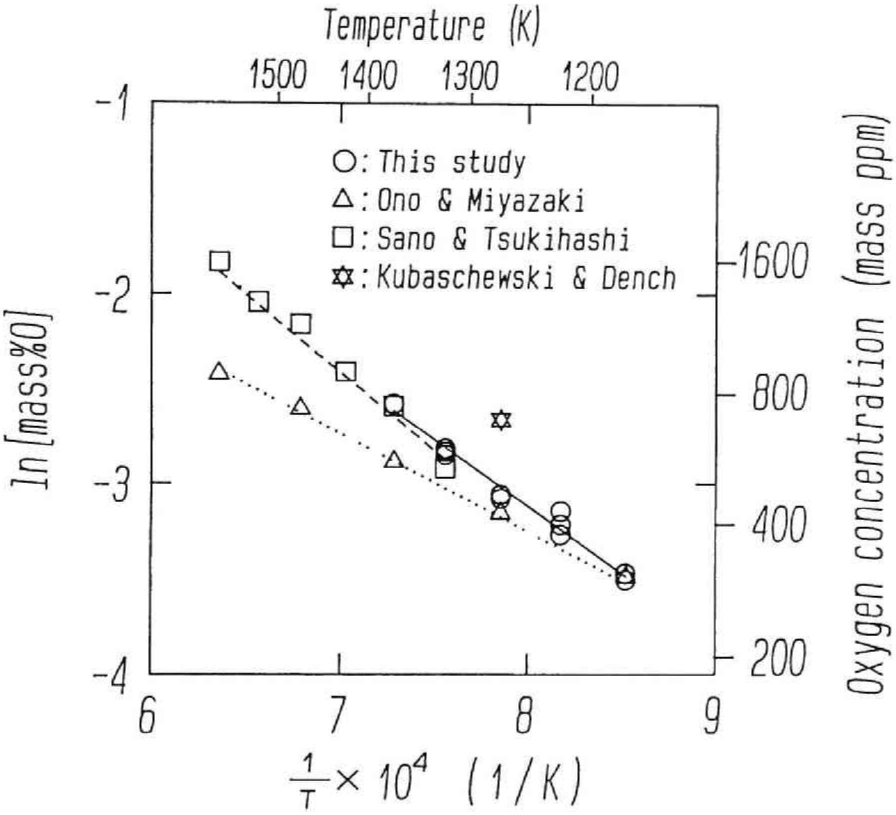

Figure 1.4: Temperature dependence of equilibrium oxygen concentration in titanium under Ca–CaO co-existence.

are somewhat low in oxygen concentration at temperatures above 1323K. A plot of data obtained by Kubaschewski and Dench[5] shows the highest value at 1273K. The oxygen concentration selected is the lowest value (700 mass ppm) among highly scattered data.

1.3.2 Calcium and Nitrogen analyses

The sample equilibrated at 1273K for 86ks contained about 1 mass ppm calcium by chemical analysis. As mentioned above, the maximum solubility of calcium in titanium at 1273K is about 60 mass ppm[4]. It seems that diffusivity of calcium in titanium is relatively low and that calcium in titanium does not equilibrate completely with calcium metal within the experimental periods.

Nitrogen concentration in the samples was independent of experimental conditions, and increased from the initial values to some extent in all cases. The values at the end of the experiments fall in the range between 340 and 1760 mass ppm randomly. The spread of values seems to result from nitrogen in calcium metal as an impurity or possibly from some leakage of the container. Table 1.1 shows, however, there was no effect on the oxygen solubilities. In the following discussion increase in nitrogen concentration was neglected and the alloys in equilibrium with calcium and calcium oxides were treated as Ti–O binary solid solution.

1.4 Discussion

1.4.1 Free energy change of dissolution of oxygen in titanium

There exist three phases, calcium, CaO and Ti–O alloy under the experimental conditions of this study. At equilibrium, the partial pressure of oxygen dissolved in titanium is equal to the partial pressure of oxygen (p_{O_2})given by the reaction,

$$\mathrm{Ca\ (l,g)} + \frac{1}{2}\mathrm{O_2}(g) = \mathrm{CaO\ (s)}. \tag{1.2}$$

The standard free energy of formation of CaO (ΔG°_{CaO}) for Eq.(1.2) is expressed by Eq.(1.3).

$$\Delta G^\circ_{\mathrm{CaO}} = RT\ln\left(\frac{p_{O_2}}{P^\circ}\right)^{\frac{1}{2}}, \tag{1.3}$$

where P° denotes 101325Pa. The free energy change of dissolution of oxygen in titanium solid solution, according to the reaction;

$$\frac{1}{2}\ O_2 = \mathrm{O}\ (\text{mass\% in Ti}) \tag{1.4}$$

can be expressed by Eq.(1.6) by using Eq.(1.3) as follows:

$$\begin{aligned} \Delta G^\circ &= -RT \ln \frac{[mass\%O]}{\sqrt{p_{O_2}/P^\circ}} && (1.5) \\ &= \Delta G^\circ_{CaO} - RT \ln[mass\%O], && (1.6) \end{aligned}$$

where $[mass\%O]$ is the oxygen concentration in mass percent. Reported values of free energy change associated with Eq.(1.4) cannot be compared directly with each other, because each author has used the different ΔG°_{CaO} values in Eq.(1.3) to calculate the free energy change of Eq.(1.4). As indicated by Wakasugi and Sano[12], there are large discrepancies among the values of ΔG°_{CaO} made by various investigators. In this study ΔG°_{CaO} which is published in JANAF[15] and is shown in Eq.(1.7), in the temperature range of 1100 to 1500K was adopted.

$$\Delta G^\circ_{\mathrm{CaO}} = -641000 + 109T \quad (\mathrm{J/mol\ O}) \quad [1100 \quad 1500\mathrm{K}] \tag{1.7}$$

As illustrated in Figure 1.4, the dependence of oxygen concentration in titanium in equilibrium with Ca and CaO on temperature can be expressed in the form;

$$\ln[mass\%O] = -\frac{7020}{T} + 2.49 \quad [1173 \quad 1373\mathrm{K}]. \tag{1.8}$$

For comparison, the data determined by Sano and Tsukihashi[4] and by Ono and Miyazaki[3] are given in Eqs.(1.9) and (1.10), respectively.

$$\ln[mass\%O] = -\frac{7970}{T} + 3.17 \quad [1373 \quad 1573\mathrm{K}]. \tag{1.9}$$

$$\ln[mass\%O] = -\frac{5180}{T} + 0.889 \quad [1173 \quad 1573\mathrm{K}]. \tag{1.10}$$

By substituting Eqs.(1.7) and (1.8) into Eq.(1.6), ΔG° for Eq.(1.4) can be calculated as shown by Eq.(1.11).

$$\Delta G^\circ = -583000 + 88.5T \quad (\mathrm{J/mol\ O}) \quad [1173\text{-}1373\mathrm{K}]. \tag{1.11}$$

This equation can be re-written by combining with Eq.(1.5)as follows:

$$\frac{1}{2} \ln\left(\frac{p_{O_2}}{P^\circ}\right) = \ln[mass\%O] + 10.6 - \frac{70100}{T} \quad [1173\text{-}1373\mathrm{K}] \tag{1.12}$$

1.4.2 Partial molar free energy of oxygen in titanium

The partial molar free energy of oxygen in titanium ($\Delta\overline{G}_O = RT\ln(p_{O_2})^{\frac{1}{2}}$) can be written in the form:

$$\Delta\overline{G}_O = \Delta\overline{H}_O - T\Delta\overline{S}_O. \tag{1.13}$$

The configurational part of $\Delta\overline{S}_O$ may be obtained as a function of composition by considering the existence of three interstitial sites per atom of titanium[7][10]:

$$\Delta\overline{S}^{conf} = R\ln\frac{3-4N_O}{N_O} \tag{1.14}$$

where No is the mole fraction of oxygen, and R is the gas constant. Eq.(1.13) can be re-written by Eq.(1.15).

$$\begin{aligned}\Delta\overline{G}_O &= RT\ln(p_{O_2})^{\frac{1}{2}}\\ &= \Delta\overline{H}_O - T\left(\Delta\overline{S}^{th} + R\ln\frac{3-4N_O}{N_O}\right)\end{aligned} \tag{1.15}$$

where $\Delta\overline{S}^{th}$ is the thermal part of $\Delta\overline{S}_O$. For dilute solutions at temperatures between 1173 and 1323K, it can be assumed that $\Delta\overline{H}_O$ and $\Delta\overline{S}^{th}$ are independent of concentration and change slightly with temperature. By combining Eqs.(1.7) and (1.15), $\Delta\overline{G}_O$ in β–titanium can be expressed as

$$-641000 + 109T = \Delta\overline{H}_O - T\left(\Delta\overline{S}^{th} + R\ln\frac{3-4N_O}{N_O}\right) \tag{1.16}$$

Assuming

$$\ln\frac{3-4N_O}{N_O} = \ln\frac{3}{N_O} \tag{1.17}$$

and

$$[mass\%O] = \frac{N_O \times 16 \times 100}{47.9}, \tag{1.18}$$

one can obtain Eq.(1.19),

$$\Delta\overline{H}_O - T\Delta\overline{S}^{th} = -583000 + 127T \quad [1173 \quad 1373\mathrm{K}] \tag{1.19}$$

$\Delta\overline{H}_O$ and $\Delta\overline{S}^{th}$ in Eq.(1.19) correspond to -583000 J/mol O and -127 J/mol O, respectively, by neglecting the small temperature dependence of $\Delta\overline{H}_O$ and $\Delta\overline{S}_O$.

These constant values are the average values within the temperature and oxygen concentration ranges in this study.

As mentioned above Tetot *et al.*[11] directly measured $\Delta\overline{H}_O$ at 1323K and determined the value, $\Delta\overline{H}_O = -627000$ J /mol O. The difference with our data is considerably large. Assuming that $\Delta\overline{H}_O$ obtained by Tetot *et al.* is constant within the temperature range 1173 – 1373K, the temperature dependence of the equilibrium oxygen concentration in β–titanium under Ca and CaO co–existence can be calculated by substituting $\Delta\overline{H}_O = -627000$ J/mol O into Eq.(1.16). By making the same approximations used in Eq.(1.19), one can obtain Eq.(1.20),

$$\ln[mass\%O] = -\frac{1740}{T} + C \tag{1.20}$$

where C is a constant which cannot be determined by ΔG°_{CaO} and $\Delta\overline{H}_O$ at 1323K. The calculated value using Eq.(1.20) rather small compared to the value in Eq.(1.8). In other words, the temperature dependence of oxygen concentration in titanium calculated from Eq.(1.20) is very small compared to that determined in this study. This difference cannot be explained at this stage.

1.5 Conclusions

Thermodynamic properties of oxygen in β–titanium–oxygen alloys were determined by equilibrating titanium–oxygen alloys with calcium and CaO at temperatures between 1173K and 1373K. From the analyzed oxygen content in titanium, the partial molar free energies of formation of oxygen in β–titanium were calculated by using the standard free energy of formation of CaO. A relationship involving oxygen potential, temperature and concentration of oxygen in the β–titanium was determined as follows;

$$\begin{aligned}
RT\ln\left(\frac{p_{O_2}}{101325\mathrm{Pa}}\right)^{\frac{1}{2}} &= -583000 - T\left(-127 + R\ln\frac{3-4N_O}{N_O}\right)\\
&\quad or\\
\frac{1}{2}\ln\left(\frac{p_{O_2}}{101325\mathrm{Pa}}\right) &= \ln[mass\%O] + 10.6 - \frac{70100}{T}\\
&\qquad [1173 - 1373K]
\end{aligned}$$

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Chapter 2

Preparation of Extra-Low-Oxygen Titanium by Calcium–Halide Flux Deoxidation

2.1 Introduction

It has been fifty years since Kroll [1][2] produced low–oxygen ductile titanium by reducing $TiCl_4$ with metallic magnesium. The mass–produced titanium by the Kroll method contains at least several hundred mass ppm oxygen, since there is technical limit for purification of feed materials and for gas–tightness of the reaction chamber. Oxygen removal from titanium containing several hundred mass ppm oxygen by metallic magnesium is nearly impossible because equilibrium oxygen concentration in solid titanium is 2.3 mass% at 1273K under coexistence of magnesium and its oxide. Furthermore, oxygen contamination is inevitable during subsequent processing, such as melting, because there is no effective deoxidation process developed in the Kroll process.

For the further purification, the iodide–process [3][4] is applied to refine titanium obtained by the Kroll method. This process utilizes dissociation of TiI_4 by a disproportionation reaction, and can produce high purity titanium containing several tens mass ppm oxygen [1]. Electrorefining [2] is also one of the effective method to produce high purity titanium, whereas the major impurity of the titanium is oxygen

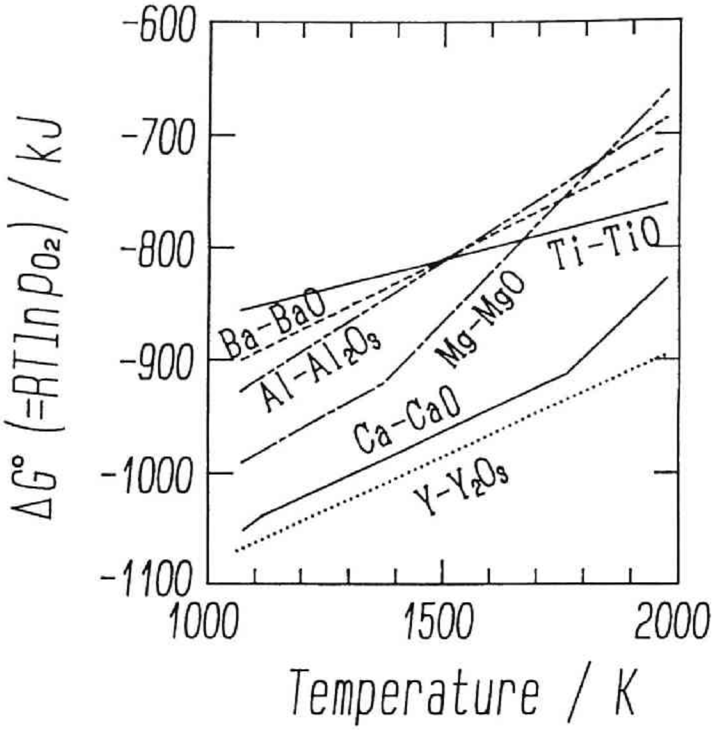

Figure 2.1: Standard free energy of formation of oxides as a function of temperature[7].

at about 100 ppmO. Continuous efforts to develop effective process for producing high purity titanium as electronic material are being made by many companies in recent years. Until today, oxygen removal directly from titanium solid solution is deemed to be very difficult and 50 mass ppm is thought to be the technical limit of oxygen removal.

The standard free energy of formation of oxide gives us a good measure to know what kind of elements can reduce titanium oxide and also deoxidize titanium to the lower oxygen contents. The standard free energy of formation of the selected oxides are shown in Figure 2.1[7], and the figure shows that barium, aluminum, calcium and yttrium can reduce TiO to metal. These metals, therefore, can be candidates for deoxidants.

From Figure 2.1, it can be seen that yttrium is one of the prominent reducing agents, but the standard free energy of formation of Y_2O_3 is not sufficiently lower than CaO from the view point of preparing low-oxygen titanium. Furthermore, yttrium metal is not suitable as deoxidant because the maximum solid solubility of yttrium in titanium is about 5000 mass ppm at 1273K[8] and because there is no effective method for removal of yttrium oxide. Aluminum and other rare–earth metal are also omitted from the candidates for similar reasons.

Metallic calcium may be the most prominent reductant, because solubility of calcium in titanium at 1273K is negligibly small as mentioned in the previous chapter, and because calcium and its oxide can be removed easily by acid leaching. Furthermore, it has relatively low melting point (1112K), and its equilibrium vapor pressure is high enough to diffuse into liquid flux at around 1300K. Furthermore, metallic calcium can be produced at a relatively low cost.

In the previous chapter, it has revealed that titanium containing 500 mass ppmO equilibrates with calcium and its oxide at 1273K as shown in Figure 2.2. This figure indicates that the deoxidation limit of the titanium by calcium is several hundred mass ppmO in the condition that activity of calcium and CaO are unity.

An advanced titanium deoxidation method was investigated in this chapter with the purpose of producing extra–low–oxygen titanium, and the feasibility of deoxidation of titanium using various fluxes was examined by employing some alkaline earth halide fused salts.

2.2 Principles

2.2.1 Principle of deoxidation

During deoxidation, oxygen in titanium solid solution reacts with metallic calcium until the equilibrium is reached, in which the partial pressure of oxygen of the titanium–oxygen alloy is equal to the partial pressure of oxygen fixed by coexistence of calcium and CaO. This reaction is given as follows,

$$[\mathrm{O}]\ (\mathrm{in\ Ti}) + \mathrm{Ca}\ (\mathrm{l\ or\ g}) = \mathrm{CaO}\ (\mathrm{s\ or\ l}) \tag{2.1}$$

where [O] (in Ti) indicates interstitially dissolved oxygen in titanium. The standard free energy change of the reaction is,

$$\begin{aligned} \Delta G^\circ_{CaO} &= -RT\ln K && (2.2)\\ &= -RT\ln\frac{a_{CaO}}{a_{Ca}\cdot a_{OinTi}} && (2.3) \end{aligned}$$

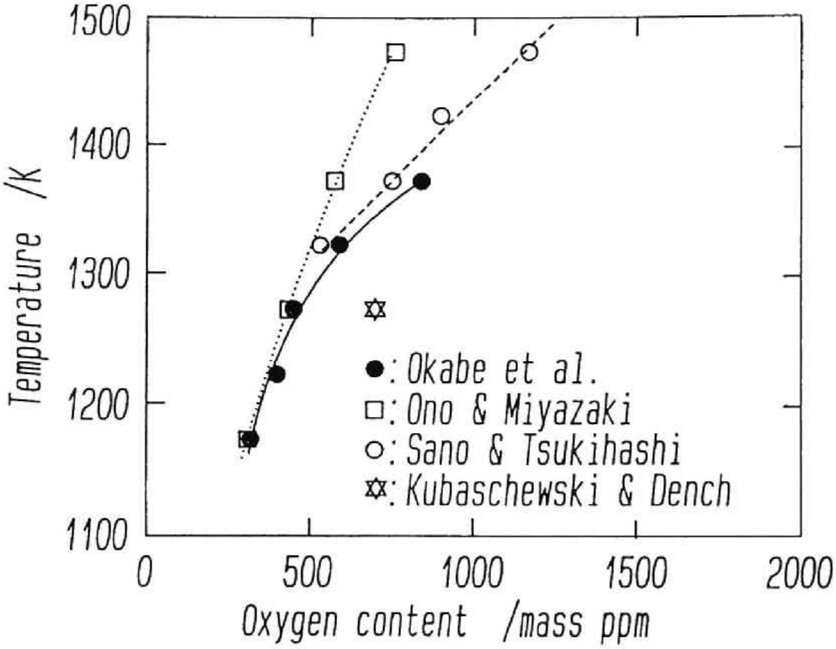

Figure 2.2: Equilibrium oxygen concentration in titanium under Ca–CaO coexistence.

where K is the equilibrium constant at a given temperature T, and a_{Ca}, a_{CaO} and a_{OinTi} are the activity of calcium, calcium–oxide(CaO) and oxygen, respectively.

Equilibrium oxygen concentration in titanium, N_O (in mole fraction), under a fixed calcium and CaO activity is expressed as follows,

$$N_O = \frac{a_{CaO}}{a_{Ca}} \cdot \frac{1}{r_O} \exp(\frac{\Delta G^{\circ}_{CaO}}{RT}) \tag{2.4}$$

where r_O is the activity coefficient of oxygen in titanium.

To attain lower equilibrium oxygen concentration in titanium under calcium existence, that is to attain lower theoretical deoxidation limit by calcium, following remarks are led from the Equation (2.4).

1. Lowering a_{CaO} by removing by–product CaO, by making compounds with CaO, or by making solutions with CaO.
2. Increasing r_O by adding a third element into titanium.
3. Changing equilibrium temperature to decrease the value of $\Delta G^{\circ}_{CaO}/RT$.

Some possibilities for effective deoxidation can be derived from these remarks. In the first place, the method by decreasing the activity of reaction product CaO in the presence of calcium metal seems to be the most promising way to lower the theoretical deoxidation limit of titanium.

As the second method, which utilizes increment of activity coefficient of oxygen in titanium, is theoretically possible by adding a third element such as hydrogen into titanium. According to Hepworth[9], hydrogen stabilizes beta–phase and increases oxygen activity coefficient. This method, however, needs further process for the removal of the added third element. Degree of increment of the oxygen activity coefficient by addition of the third element is, in general, not sufficiently high compared to that of decrement of CaO activity using fluxes, therefore, it seems less effective than the first method.

The third method can be possible by lowering the reaction temperature according to the result obtained in the previous chapter. This method is, however, not practical because it takes long time to diffuse oxygen out of titanium at temperature below 1200K.

From these reasons, the first method, which decreases the activity of CaO, was adopted for deoxidation of titanium in this study.

2.2.2 Selection of deoxidation fluxes

While there are several ways to decrease the activity of CaO, the use of liquid fluxes, such as alkaline-earth halide flux, were considered in this study to obtain extra-low-oxygen titanium. Because a large amount of CaO dissolve, in general, in these fluxes, hence, activity of CaO can be decreased by diluting CaO in the flux.

In the selection of suitable flux for deoxidation, the halide fluxes would have to be satisfied the following conditions.

a. Liquid state at deoxidation temperature to facilitate deoxidation.

b. Inert and insoluble with titanium.

c. Dissolves CaO, and decreases activity of CaO.

d. Stable under existence of metallic calcium.

e. Dissolves deoxidant metallic calcium to some extent.

Under these conditions many compounds suitable for the flux were screened from the standpoint of the reported phase diagrams[10], and some calcium–halide and barium–halide fluxes were nominated in this study. In addition to the limitation above mentioned, the following terms are desirable for the effective deoxidation.

I. Large solubility of CaO in the flux at temperature range 1100K– 1300K.

II. Small solubility of calcium in the flux, and vice versa, in order to keep the activity of calcium as high as possible.

III. Containing few impurities especially oxide, hydrate and carbonate which react with metallic calcium during deoxidation to form CaO in the flux.

Taking into account of these terms, calcium chloride ($CaCl_2$) was selected as the most preferable flux. As shown in Figure 2.3 [11], CaO dissolves into $CaCl_2$ up to about 20 mol % in the temperature range 1100K–1300K. Whereas the solubility of $CaCl_2$ in calcium is less than 1 mol % as shown in Figure 2.4 [12]. Therefore calcium saturated $CaCl_2$ flux, in which calcium activity is nearly unity, is expected to be suitable for deoxidation of titanium and can decrease the activity of the reaction-product CaO effectively.

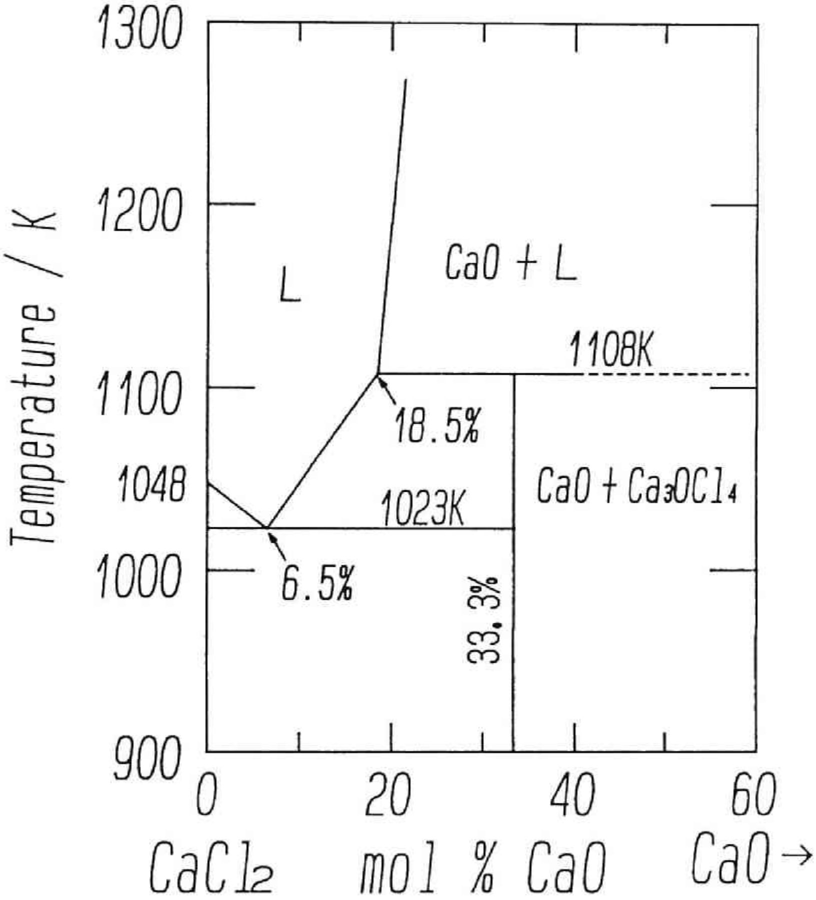

Figure 2.3: Phase diagram of the $CaCl_2$–CaO system [11].

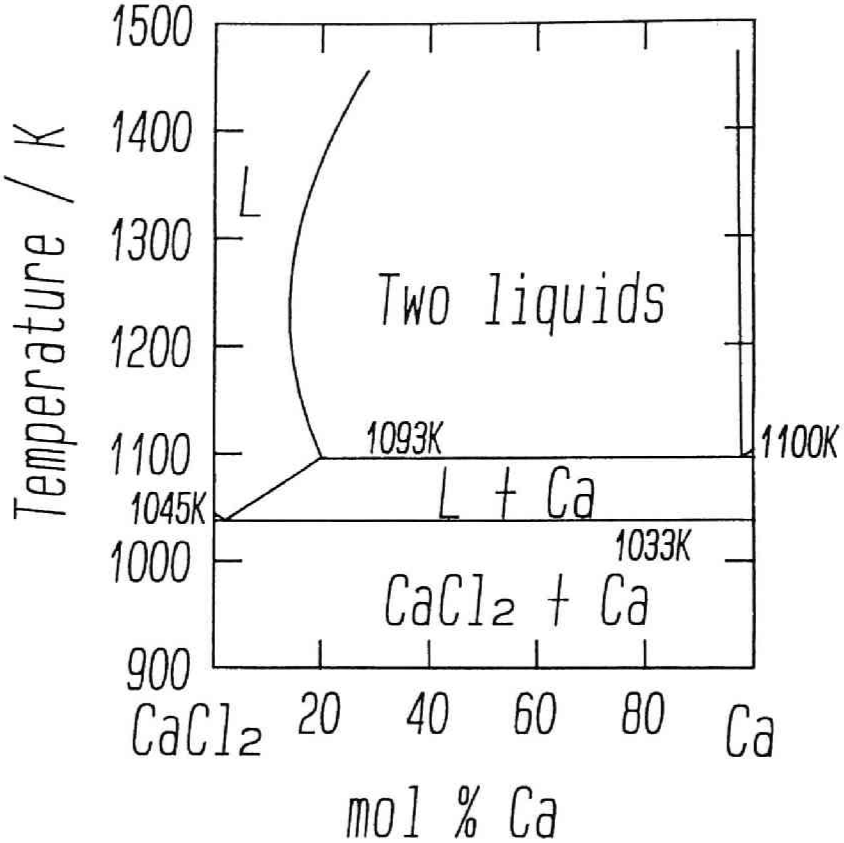

Figure 2.4: Phase diagram of the Ca–$CaCl_2$ system [12].

The commercially available $CaCl_2$ contains much water and a small amount of CaO or $CaCO_3$ as impurities. The amount of oxygen in $CaCl_2$ affects on the deoxidation limit of titanium. Therefore, it is preferable to use $CaCl_2$ not containing such oxygen–containing impurities. $BaCl_2$ was also used as a flux because it is less hygroscopic than $CaCl_2$.

As an alternate method, oxide containing flux, $CaCl_2$–Y_2O_3 in this study, was examined as effective deoxidation. As shown in Figure 2.1, Y_2O_3 is the one of the stable oxides which is not reduced even by calcium. Addition of small pellet of Y_2O_3 into the $CaCl_2$ flux, therefore, have some possibilities to reduce a_{CaO} in the flux during deoxidation by forming complex oxides of CaO and Y_2O_3. From JCPDS[13] cards, CaO is reported to form complex oxides with Y_2O_3 such as $Ca_3Y_2O_6$, CaY_2O_4 and CaY_4O_7. $CaCl_2$ was used as flux to transport reaction product CaO to form complex oxides with the Y_2O_3 pellet which is set apart from titanium with the purpose of eliminating contamination of yttrium into titanium.

2.3 Experimental

2.3.1 Flux preparation

The raw materials used for preparing the flux were, anhydrous calcium chloride (99.9%), barium chloride (99.9%) in powder form, and calcium (98%) in nodular form: main impurities of these were their oxides and hydrates.

In some experiments the calcium chloride was used as received, but in the others the calcium chloride and barium chloride were kept in a vacuum at 500K for 90ks (24 hours) to remove adsorbed water and hydrate before use.

$CaCl_2$–Y_2O_3 flux was prepared simply by mixing $CaCl_2$ powder and Y_2O_3 pellet which is press–formed from powder.

2.3.2 Experimental procedures

Several kinds of titanium containing different amounts of oxygen were reacted with the flux in a reaction vessel. These titanium samples were the same that used

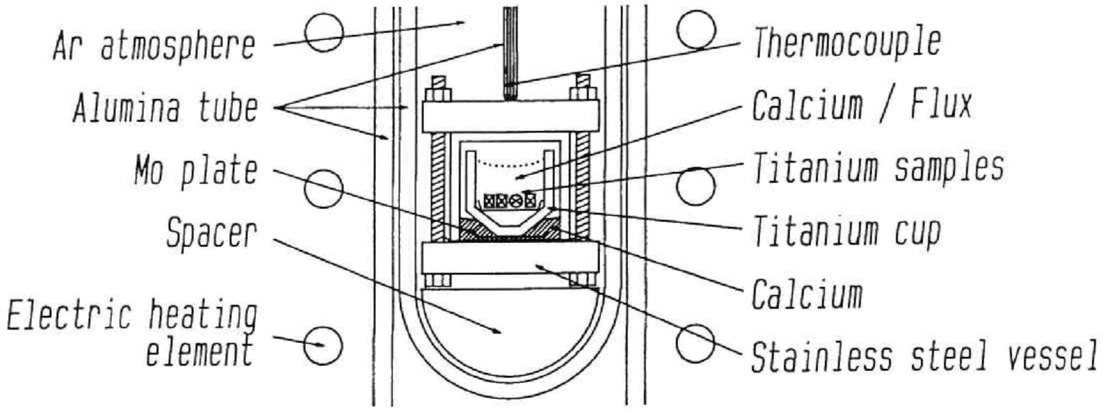

Figure 2.5: Schematic illustration of the experimental apparatus.

in Part 1. The apparatus and experimental method have been described in Part 1, and only a brief outline will be given here.

Figure 2.5 illustrates the reaction vessel arrangement used for the deoxidation. 10 to 15 pieces of titanium samples (0.1g each) were placed on a titanium dish in the titanium cup. The reducing agent, calcium(1–2g) in nodular form, was put on the bottom of the vessel and, in some cases, also in the cup. The flux(5–8g), such as $CaCl_2$, $BaCl_2$ or $CaCl_2$–Y_2O_3, was also filled in the cup.

The assembled reaction vessel was heated up to 1173–1273K and kept in the furnace for 90ks. The amount of time necessary to reach equilibrium has been determined in the previous chapter. After equilibrium, the reaction vessel was quenched into water. The vessel was opened to make certain that calcium metal remained in the vessel and that there was no leakage of the vessel. The molten flux was removed from the samples by dipping the titanium cup in an aqueous acetic acid solution. The identification of the phases existing in the flux were carried out by X-ray diffractometry, and the results were compared with JCPDS cards[13].

The obtained glossy titanium samples were carefully washed with an acid (0.81 mol/kg HF, 0.42mol/kg HNO_3 aqueous solution), and submitted to oxygen analysis by an inert gas fusion method. Most of the samples were analyzed by some companies specialized in this technique.

2.4 Results and Discussions

2.4.1 Observation of the flux

After the deoxidation experiment, the titanium cup which normally adhered to the reaction vessel with calcium was pulled apart from the vessel. No metallic calcium was observed on a fused salts. The color of the solidified $CaCl_2$ flux and $BaCl_2$ flux were changed to gray–green and gray, respectively, which were originally white.

No phases other than $CaCl_2$, CaO and their hydrate were detected in the as–cooled $CaCl_2$ flux by X–ray diffractometry. The $CaCl_2$ flux reacted vigorously with aqueous CH_3COOH solution and it was completely dissolved within 3.6ks, whereas the $BaCl_2$ flux was less soluble than $CaCl_2$ flux in the aqueous acid solution. It took more than 30ks (8hr.) to dissolve it in the aqueous CH_3COOH solution.

2.4.2 Deoxidation by using $CaCl_2$ flux

Experimental details and analytical results for the oxygen concentrations in titanium before and after experiments are listed in Table 2.1.

The final oxygen concentration were essentially independent of the initial oxygen concentrations in these experimental conditions. The reaction periods, therefore, appear to be sufficient in these experimental conditions. At temperatures between 1173 and 1273K, reaction temperatures were also found to be ineffective to the final oxygen concentration.

In the column "conditions" in Table 2.1, the $\langle Ca : Liquid \rangle$ denotes the state of the reductant which was supplied to the flux: this is represented schematically in Figure 2.6. In case (b) in Figure 2.6, both calcium and the sample were put in the titanium cup with the flux. On account of the strong affinity of the calcium with

Table 2.1: Experimental conditions and results of oxygen analyses of deoxidized titanium.

Exp. No.	Conditions Flux Temperature Holding time	Oxygen content (mass ppm) Initial	 After deoxidation
1	Ca-$CaCl_2$ 1173K 220ks <Ca: Liquid>	200 720 1200 1270	30 40, 80 70, 100 60
2	Ca-$CaCl_2$ 1223K 130ks <Ca: Liquid>	200 720 1200	40, 90 30, 80 70, 90
3	Ca-$CaCl_2$ 1273K 86ks <Ca: Liquid>	200 720	70, 90 70, 80
4	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor>	200 720 1200	60, 70, 70 40 60
5	Ca-$CaCl_2$ 1273K 65ks <Ca: Vapor>	200 720	60, 70 40, 40, 60. 60, 70
6	Ca-$CaCl_2$ 1273K 65ks <Ca: Vapor>	200 720	60, 80 30. 50. 60. 60, 70. 80
7	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor> [vacuum dried flux]	200 720	70 60, 70, 70, 70
8	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor> [double deoxidation]	(200) (720)	60. 70 70. 70. 70
9	Ca-$BaCl_2$ 1273K 86ks <Ca: vapor>	200 720	200 200. 220. 230
10	Ca-$CaCl_2$-Y_2O_3 1273K 50ks <Ca: liquid>	200 720 1200	180. 180. 290. 330 390 490
11	Ca-$CaCl_2$-Y_2O_3 1273K 86ks <Ca: liquid>	200 440 1200 1430	210. 230. 310. 360 220 240. 370. 390 300

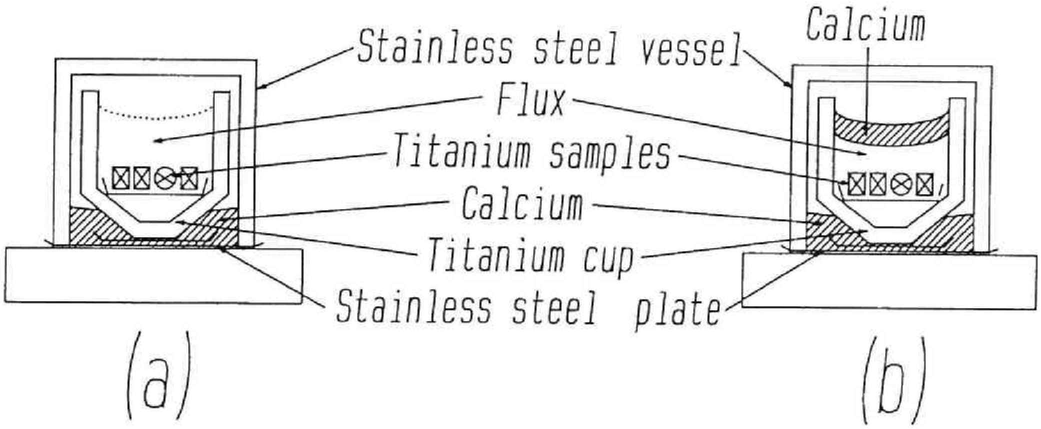

Figure 2.6: Reaction vessel arrangement

oxygen or/and water, it seems impossible to prevent CaO contamination from the surface of calcium granule into the flux in case that calcium granules were mixed with flux. However, as can be seen in Exp. No. 1,2 and 3, titanium samples were deoxidized to the level below 100 mass ppm oxygen.

In another case as illustrated by (a) in Figure 2.6, only $CaCl_2$ and titanium samples were put in the titanium cup, and metallic calcium was isolated from the samples. As vapor pressure of calcium is high enough (about 1.8kPa)[7] to diffuse to the sample through the flux, the deoxidant was supplied in vapor form from the bottom of the reaction vessel. In this case, impurities in metallic calcium, e.g. CaO[14], does not contaminate the flux, and the volatile impurities in the flux, such as water, will be gettered by the calcium as temperature raises. Therefore, deoxidation in the condition of $\langle Ca : Vapor \rangle$ is expected to be more favorable than that of $\langle Ca : Liquid \rangle$, because it contains less CaO than the flux mixed with metallic calcium. Contrary to the prediction, the results of Exp. No.4,5 and 6 in Table 2.1 show no significant difference in oxygen concentrations compared to that of Exp.No.1,2 and 3. This result indicates that impurities in calcium have no influence on final oxygen concentration. $CaCl_2$ used in this study, therefore, contained the larger amount of CaO as impurity than the calcium granules.

In Exp.No.7 in Table 2.1, $CaCl_2$ flux is vacuum dried at 500K for 90ks to remove adsorbed water and hydrate beforehand, and used as a flux. In Exp.No.8, titanium samples and cup which is previously deoxidized in Exp.No.6 were again subjected to deoxidation, with the purpose of eliminating the influence of oxygen in the titanium samples and cup. The final oxygen concentrations were in both cases around 70 mass ppm, and this deoxidation limit is probably decided by CaO preliminarily contained in the $CaCl_2$ starting material.

The difference between the analytical oxygen concentrations for the samples below 100 mass ppm can not be fully discussed at this stage because analytical accuracy of oxygen concentration in this level is not enough to discuss the difference of experimental conditions.

2.4.3 Deoxidation by using $BaCl_2$ flux

In Exp.No.9 in Table 2.1, 10g of dried $BaCl_2$ flux was used instead of $CaCl_2$, and samples were deoxidized by 6g of calcium which is supplied in vapor form. $BaCl_2$ was reported to be less hydroscopic flux than $CaCl_2$, that is, oxygen in the initial flux seems to be lower than that in $CaCl_2$ flux. However, the oxygen concentrations of the samples after deoxidation were about 200 mass ppm. It was concluded that $BaCl_2$ flux was less effective for deoxidation than $CaCl_2$ flux.

As $BaCl_2$ may be reduced to the metallic barium by calcium, following reaction between $BaCl_2$ and calcium have to be taken into consideration.

$$BaCl_2 + Ca = Ba + CaCl_2. \tag{2.5}$$

According to MALT[15], the equilibrium constant of the Equation (2.5) is 0.958×10^{-2} at 1273K. Composition of Ca–Ba alloy after deoxidation, which is formed by the deoxidant calcium and barium from reduced $BaCl_2$ flux, depends on the initial amount of $BaCl_2$ and calcium. Assuming that reduced barium dissolves ideally in liquid calcium and that $BaCl_2$ and $CaCl_2$ makes an ideal solution at 1273K, large mass of $BaCl_2$ (viz. dilute $CaCl_2$) flux would equilibrate with calcium rich–barium alloy in this experimental condition. This fact indicates $BaCl_2$ is one of the compatible fluxes for deoxidation which can coexist with metallic calcium.

By X–ray diffraction measurements, only $BaCl_2$ was identified in the flux after deoxidation. Because of lack of CaO–$BaCl_2$ phase diagram, the solubility of CaO in $BaCl_2$ can not be evaluated. Since many halides have some solubilities of CaO, at least several mol % CaO is expected to dissolve in $BaCl_2$. The result tabulated in Exp.9, however, indicates that the activity of CaO in $BaCl_2$ was not as low as that in $CaCl_2$, and that $BaCl_2$ was not necessarily appropriate flux for the deoxidation of titanium.

2.4.4 Deoxidation by using $CaCl_2$–Y_2O_3 flux

In Exp.No.10 and 11 in Table 2.1, 8g of 93mol% $CaCl_2$–7mol% Y_2O_3 flux was used with expectation of forming stable complex oxides between CaO and Y_2O_3. The analyzed values in Exp.10 and 11, however, indicate that use of $CaCl_2$–Y_2O_3 flux was not effective than $CaCl_2$ single use. After rinsing the flux by acetic acid, the black particles remained undissolved. No phases except Y_2O_3 were found by X–ray diffraction measurements in that black particles. The activity of CaO, therefore, could not decreased by Y_2O_3 under the conditions used in this experiment.

2.4.5 Development of further effective flux for deoxidation

For the development of the further effective flux for deoxidation to the level below 10 mass ppm, the flux which lowers the activity of CaO to one–hundredth level is needed. At this stage, $CaCl_2$ seems to be the most prominent flux because of its solubility of CaO, its stability with calcium and so on. The most serious drawback of the $CaCl_2$ is its purity due to the hygroscopicity of $CaCl_2$.

There exist many halide fluxes such as CaF_2 which is compatible with calcium. However, there are few available fluxes considering that their melting points or vapor pressures. CaF_2 is one of the purest halides which can be easily obtained commercially and are nonabsorptive. As CaO and CaF_2 are insoluble with each other below 1600K as shown in Figure 2.7 [16], CaF_2 for single use is not suitable for the deoxidation at temperature range 1173– 1373K. Nevertheless, CaF_2 might be used as $CaCl_2$–CaF_2 flux or BaF_2–CaF_2 flux because the addition of $CaCl_2$ or BaF_2 decreases fusing point of these fluxes[17].

Figure 2.8 shows the qualitative phase diagram of the $CaCl_2$–CaF_2–CaO system at 1273K, which was estimated by using three binary phase diagrams[11][16][17]. According to Figure 2.8, the solubility of CaO changes little in the $CaCl_2$ rich–CaF_2 liquid region, and decreases with increasing solid CaF_2 content in the flux. That is, $CaCl_2$–50 mol%CaF_2 liquid flux seems to have as same solubility as pure $CaCl_2$ flux.

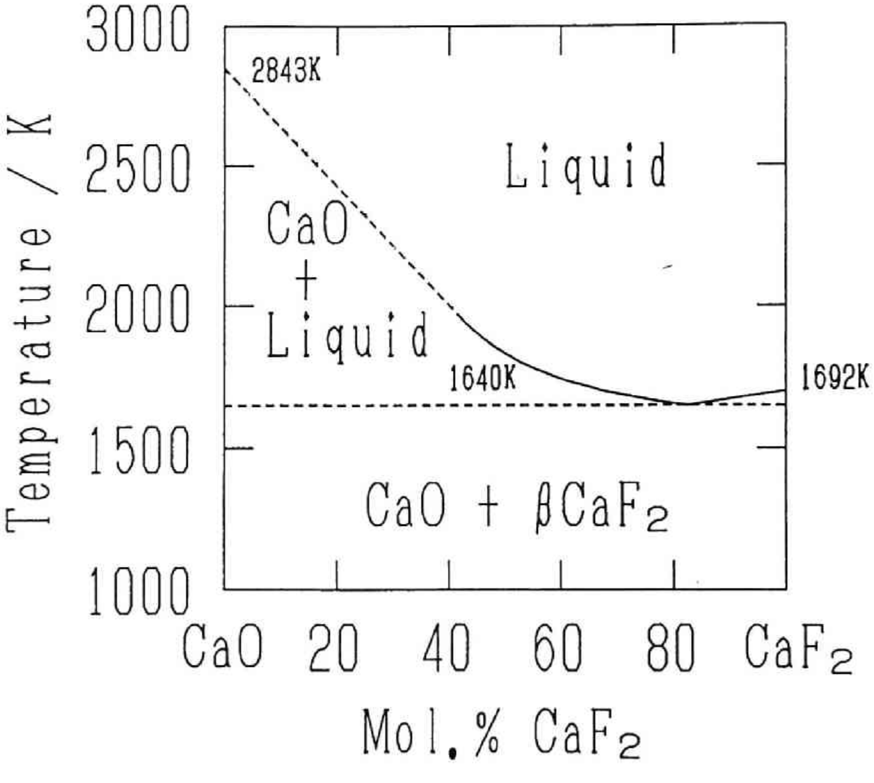

Figure 2.7: Phase diagram of the CaF_2–CaO system [16].

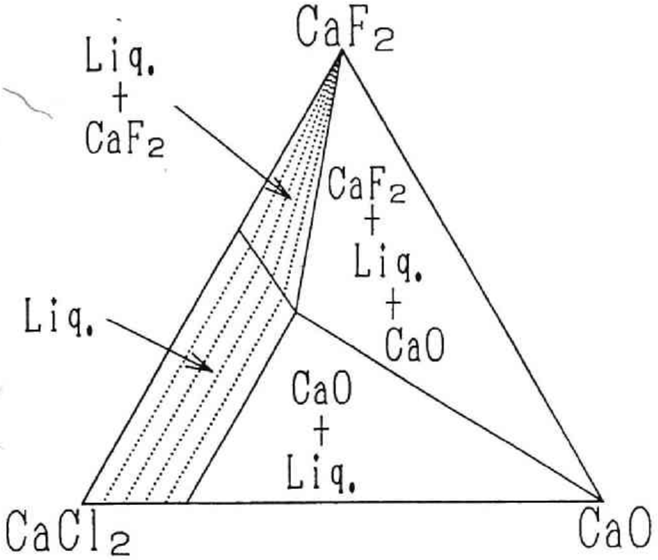

Figure 2.8: Qualitative phase diagram of the $CaCl_2$–CaF_2–CaO system at 1273K. Isoactivity lines for CaO are drawn as dotted lines

This flux probably contain less CaO as impurity because of inertness and cleanliness of CaF_2, and it seems as effective as the $CaCl_2$ flux considering the solubility of CaO.

For the further development of titanium deoxidation by using these mixed halides fluxes, the accurate oxygen analysis has to be established. In addition, a method to determine the activity of CaO in the flux is desired.

2.5 Conclusions

The advanced deoxidation methods of titanium were examined from the thermodynamic view point to attain the lower oxygen level.

Deoxidation of titanium by calcium at around 1273K was carried out, and some halide flux was used in this study with the purpose of decreasing CaO activity. Titanium wires and small pieces containing several hundreds mass ppmO was deoxidized as low as a few tens mass ppmO by using Ca–$CaCl_2$ flux at 1273K.

The oxygen sources to make worse the efficiency of the further deoxidation of titanium were discussed, and one of them was suggested to be the oxygen contamination in the flux. CaO contamination due to the reductant and adsorbed water were minimized by using calcium vapor and by flux pre–treatment.

Ca–$BaCl_2$ flux and Ca–$CaCl_2$–Y_2O_3 flux were found to be less effective than $CaCl_2$ flux for deoxidation of titanium.

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Chapter 3

Characterization of Extra-Low-Oxygen Titanium

3.1 Introduction

Over the past several years, the demand for high purity titanium for use in electronic materials has increased. For applications such as target materials for semiconductor uses, 4 to 5N (excluding gaseous elements) high purity Kroll titanium has been mainly employed. More recently, for electronic material use titanium is purified further by using method of the iodide process [1] or electrolytic refining [2]. As shown in Table 3.1, the level of purity of titanium produced in these ways is between 5 and 6N (excluding gaseous elements), with the major impurity of 6N titanium being oxygen at about 100 mass ppm.

Among the known purification processes (e.g. electrolysis in molten salts, electron beam floating zone melting, electro–transport, and degassing in ultra high vacuum), no effective methods other than electrolytic refining and iodide refining have been developed for oxygen removal to a level below 50 mass ppm. Even if low oxygen titanium is successfully produced using these optimized methods, contamination by oxygen is inevitable during subsequent processing, such as during electron beam melting.

Oxygen removal directly from titanium–oxygen solid solution to a level below 50 mass ppm is deemed to be very difficult because titanium has a strong affinity for oxygen. For this reason the titanium refining process is based on reaction of oxygen free titanium compounds in a gas–tight system. From a thermodynamic view point,

Table 3.1: Some analytical values of high purity titanium for electronic material use.

Manufacturer	Grade*	Impurity concentration in titanium (mass ppm)									
		Fe	Ni	Cr	Na	K	U	Th	C	N	O
A	4N8	5	<1	3	<.1	<.1	<.001	<.01	30	10	<200
B	4N5	3	<1	<1	<.005	<.005	<.001	<.001	15	34	240
	4Nup	4	16	8	<.1	<.1	<.001	<.001	39	39	70
C	5N	1	<1	1	<.1	<.1					400
D	4N	30	10	10	.1	.1	.001	.001	30	30	400
	5N	2	<.1	.2	<.002	<.004	<.001	<.001		10	100
E	5N5	<1	<1	<1	<.03	<.05	<.001	<.001	<50		<200
	6N	<.1		<.1	<.02	<.02	<.0005	<.0005	<10		120
F	5N	3.7	0.045	0.16	<0.015	<0.010	<0.0002	<0.0002	9.3	41	159

* : Excluding carbon and gaseous elements.

external gettering used for solid state refining is one of the most promising methods for direct deoxidation of titanium, and the feasibility of deoxidation of titanium was shown in the previous chapter. This method can be applied to the final deoxidation of titanium products as a surface deoxidation treatment following machining.

In this chapter, titanium deoxidation by reaction with a chemically active element, namely calcium dissolved in $CaCl_2$ through surface contact, was examined in the temperature range 1273 to 1473K, to obtain extra–low–oxygen titanium. And characterization of the deoxidized titanium was carried out.

Calcium is thought to be the most effective deoxidation agent not only because it has an extremely strong affinity for oxygen but because it has a high vapor pressure around 1273K (P_{Ca}=1.9kPa)[3] and can diffuse into $CaCl_2$. Furthermore the maximum solubility of calcium in titanium is reported to be only about 60 mass ppm at 1273K [4]. $CaCl_2$ was used as a flux to contain the deoxidation agent calcium and in addition, to facilitate the reaction by diluting the reaction product CaO, i.e., decreasing the activity of the by–product CaO.

Since the principle of calcium–halide flux deoxidation of titanium is reported in detail in the previous chapter only a brief outline will be given here. Titanium–oxygen solid solution can be deoxidized by calcium to a lower oxygen level by the following reaction:

$$\mathrm{O\ (in\ Ti) + Ca\ (in\ flux) = CaO\ (in\ flux)} \tag{3.1}$$

Co–existence of calcium and the by–product, CaO, fixes the equilibrium oxygen partial pressure, and hence, the amount of residual oxygen in titanium is thermodynamically decided. The deoxidation limit of titanium is given in equation (3.2) at constant temperature T.

$$[mass\%O] = \left(\frac{a_{\mathrm{CaO}}}{a_{\mathrm{Ca}}}\right)\left(\frac{1}{f_{\mathrm{O}}}\right)\exp\left(\frac{\Delta G^\circ}{RT}\right) \tag{3.2}$$

where ΔG° is the standard free energy change of Equation (3.1), a_{CaO} and a_{Ca} are the activities of CaO and calcium, respectively, and f_{O} is the activity coefficient of oxygen in solid titanium. When determining the partial pressure of oxygen in β–solid titanium, the author measured the equilibrium oxygen concentration in titanium coexisting with calcium and CaO at temperatures between 1173K and 1373K in chapter 1. Based on these obtained data, and the condition that the activity of the by–product CaO is unity, the predicted deoxidation limit of titanium by using pure calcium at 1273K was 500 mass ppm as shown in Figure 3.1.

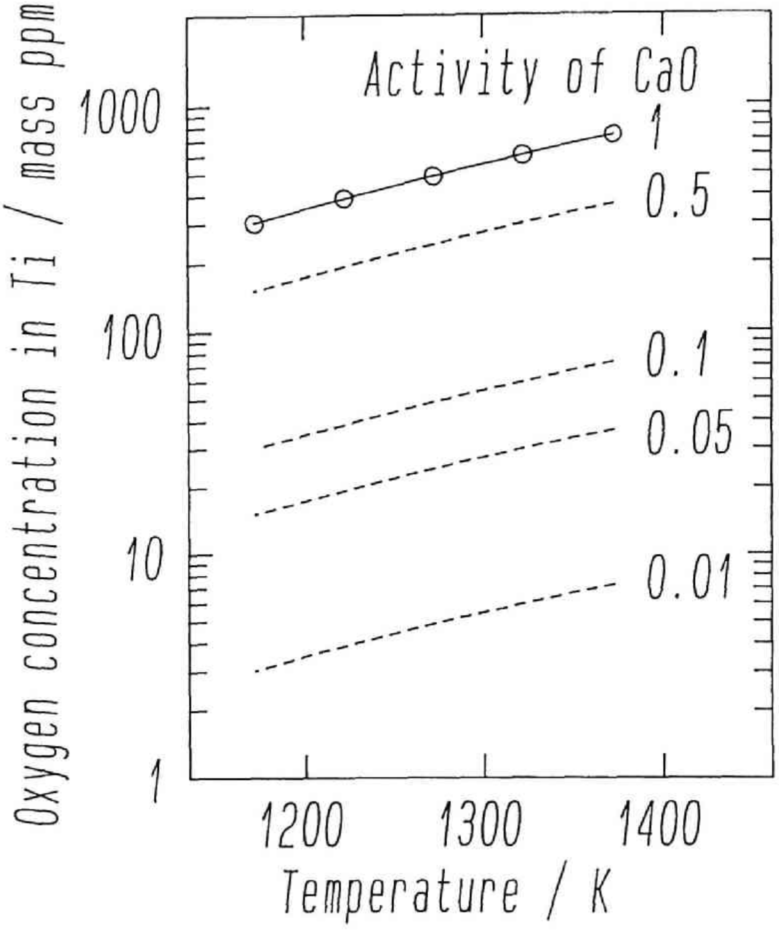

Figure 3.1: Equilibrium oxygen concentration in β–Ti under Ca existence. The curves indicate the theoretical deoxidation limits of titanium as a function of temperature and activity of CaO using calcium saturated flux. The circles (○) are the experimental data obtained in chapter 1.

In the previous chapter, the author discussed feasibility of preparation of low oxygen–containing titanium by decreasing the activity of the by–product CaO using various calcium–halide fluxes in the presence of calcium metal. Several factors have been considered in choosing a flux and the process parameters for deoxidation, and $CaCl_2$ appears to be the best flux among many halide fluxes around 1300K. $CaCl_2$ used as a flux dissolves a large amount of CaO (about 20 mol% at 1273K [5]), while the solubility of $CaCl_2$ in calcium is less than 5 mol% [6]. It is, therefore, expected that the CaO, by–product of deoxidation will be dissolved by the calcium–saturated $CaCl_2$ flux, and that the deoxidation limit will be lowered as the activity of CaO (refer to Equation (3.2)) is decreased. For example, Figure 3.1 illustrates that when the activity of CaO in the flux is decreased to a level of 0.01 in the presence of calcium, the deoxidation limit is lowered to 5 mass ppm level at 1273K.

This chapter reports the results of an experimental investigation directed towards the preparation of extra–low–oxygen titanium by using the Ca–$CaCl_2$ flux deoxidation method. Characterization of the resulting purity was made by micro Vickers hardness measurements, trace element analysis, and electrical resistivity measurements.

3.2 Experimental

Figure 3.2 shows the arrangement of the reaction tube used for titanium deoxidation in this study. Ten to fifteen titanium samples (about 0.1–2g each) were placed on a titanium dish within a titanium cup, which was filled with about 20g of $CaCl_2$. The $CaCl_2$ used in this study was reagent grade anhydrous $CaCl_2$ (99.9%) in powder form, dried at 800K for more than 200ks. As shown in Table 3.2 several kinds of titanium pieces and wires with different oxygen concentration and configuration were used as starting materials. The cup containing the titanium sample and $CaCl_2$ was sealed in a stainless steel tube with 5g of calcium granules, as shown in Figure 3.2. To avoid contamination of the sample by impurities in calcium (mainly CaO), calcium was isolated from the samples and flux, and supplied to the flux in vapor form.

The assembled sealed tube was heated in an electric furnace to a temperature between 1173 and 1473K. The holding time was between 86.4ks and 260ks, after which, the reaction tube was taken out from the furnace and quenched in water.

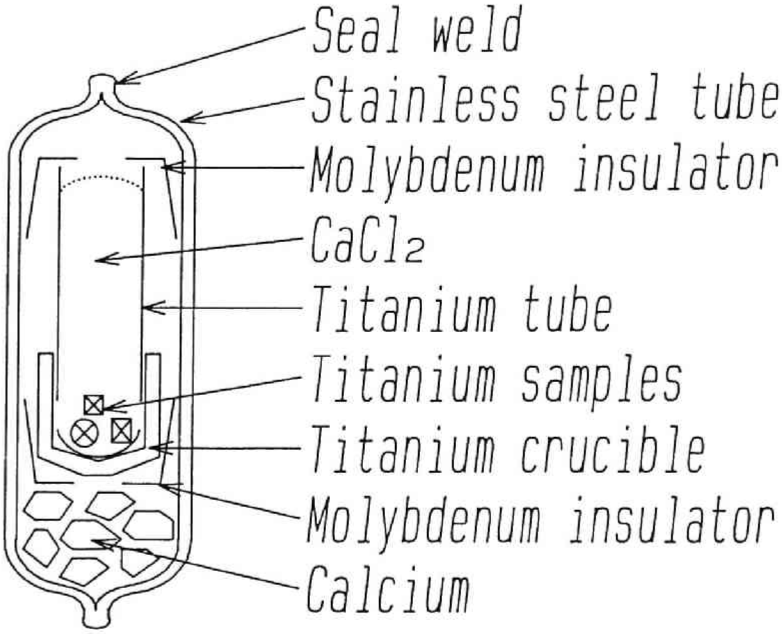

Figure 3.2: Schematic illustration of the reaction tube.

Table 3.2: Some analytical values of titanium samples (electrolytically refined sponge, electron beam-melted) used for deoxidation experiments.

Sample no.	Grade[a]	Oxygen conc.	Nitrogen conc.	RRR[b]	Hv[b]	Configuration
		(mass ppm)		$\left(\frac{\rho_{298}}{\rho_{77}}\right)$		
A	99.9999[c]	110	5	88	131	2.9 mmϕ wire
B1	99.9999[c]	130	10	27	224	1.8 mmϕ wire
B2	99.9999[c]	130	10	24	–	0.9 mmϕ wire
C	99.9999[c]	150	10	43	185	3.0 mmϕ wire
D	99.9999[c]	260	20	28	116	3.0 mmϕ wire
E	99.99[d]	200	20	–	93	small pieces
F	99.9[e]	900	100	9.3	201	1.2 mmϕ wire

a : Excluding gaseous elements.
b : Measured as received.
c : Electrolytically refined sponge.
d : E.B.–melted high purity sponge.
e : Commercial grade titanium.

The amount of time necessary to reach equilibrium was determined in previous chapter 1. In some experiments, for the purpose of annealing, the reaction container was cooled in the furnace, or quenched and then heated again to 1073K for 10ks to remove defects in the samples which would interfere in resistivity measurements. After heat treatment, the calcium-saturated fused salt in the titanium cup was removed by leaching with (1+1) acetic acid, and the resulting glossy titanium samples were carefully cleaned in warm HCl aqueous solution followed by water, alcohol and acetone, and then allowed to dry.

Oxygen and nitrogen analyses of the samples were made using an inert gas fusion infrared absorption method (LECO TC-336 analyzer). Preceding the oxygen and nitrogen analyses, the samples were chemically polished with a 1:4:10 mixture of $HF:HNO_3:H_2O$. For oxygen and nitrogen extraction, 0.1g of titanium sample enclosed in 1g of platinum foil was dropped into a graphite crucible and held at a temperature above 2500K. The average blank values (mainly due to the platinum bath) of oxygen and nitrogen were $1.8 \pm 0.2 \mu g$ and $0.2 \pm 0.1 \mu g$, respectively.

Electrical resistivity measurements were carried out on samples in wire-form which were immersed in liquid helium, liquid nitrogen, and water maintained at 298K. Schematic illustration of the cryostat used for the resistivity measurements at 4.2K is shown in Figure 3.3. The conventional four probe direct current technique was adopted using spot-welded Cu wires, 0.1mm in diameter, as potential terminals. Sample currents were in the range, 1 to 100mA, and the potential difference at the terminals of the sample, proportional to the sample resistance, was measured by a voltmeter (Keithley Model K-181 Nanovolt Detector). In order to eliminate the contribution by thermal electromotive forces, the current polarity was reversed three times, and the mean of four readings was taken as the electromotive force value.

Micro Vickers hardness measurements using a 500 g load were carried out at room temperature on the chemically polished surfaces of cross sectioned samples. The samples were mounted in resin for polishing to make the planar surfaces, and the scratches inherited from mechanical polishing were chemically removed with HNO_3-HF solution. Grain boundaries were well-etched by this acid.

Trace element analysis of titanium was carried out utilizing glow discharge mass spectroscopy(GDMS), and in the case of calcium, the values were cross checked by using flame-less atomic absorption spectroscopy.

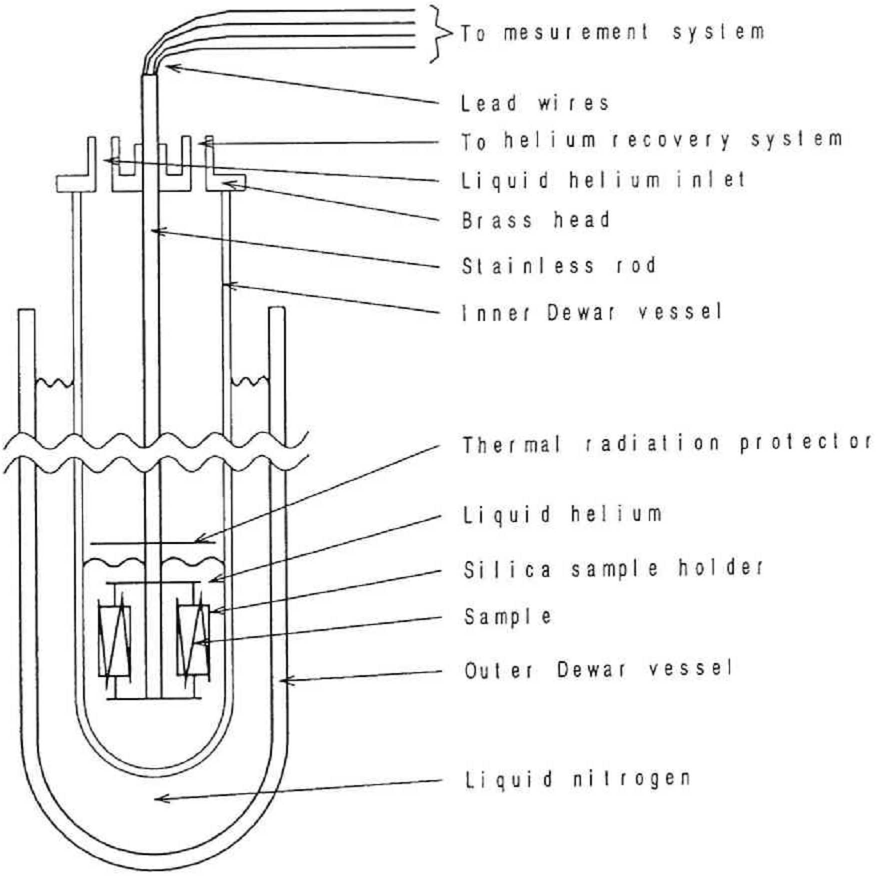

Figure 3.3: Schematic illustration of the cryostat used for the resistivity measurements at 4.2K.

3.3 Results and Discussion

3.3.1 Oxygen and nitrogen analysis

The analytical results for the oxygen and nitrogen concentrations in titanium before and after experiments are listed in Table 3.3.

By using Ca–$CaCl_2$ flux, titanium samples were deoxidized to a level below 100 mass ppm, and in some experiments the oxygen contents in titanium were lowered to less than 20 mass ppm. The final oxygen concentrations were essentially independent of the initial oxygen concentrations in these experimental conditions. The reaction periods appear to be sufficient to reach equilibrium, and thus, the deoxidation limit in these experiments may be determined from the activity of CaO in the flux. It is believed that in this study the amount of CaO derived from deoxidation of titanium in this study was small in comparison to the level of CaO impurity in $CaCl_2$. For further deoxidation, it seems necessary to refine the $CaCl_2$ for CaO elimination.

Nitrogen concentrations in the samples were independent of the experimental conditions, and increased from the initial values by about 40 mass ppm, in all cases. This increment seems to be caused by residual nitrogen in the reaction tube and/or the presence of nitrogen in the $CaCl_2$ and calcium, since no nitrogen gas elimination was done preceding the sealing of the sample in the reaction tube. As calcium has a weaker affinity for nitrogen than titanium, it is not possible to remove nitrogen from titanium by this method.

In order to produce titanium wires with no defects such as dislocations, samples in Exp.16,17,19, and 24 were annealed or cooled in the furnace following deoxidation, and then subjected to resistivity measurements. The samples of Exp.24 in Table 3.3 were heat treated using Ca–CaO flux at 1273K for the purpose of producing titanium wire containing 500 mass ppm oxygen with the same nitrogen concentration as the others.

3.3.2 Micro Vickers hardness measurements

Results of the micro Vickers hardness measurements are listed in the final column of Table 3.3. These values are plotted against oxygen concentration in Figure 3.4.

Table 3.3: Results of oxygen and nitrogen analyses of titanium samples deoxidized using Ca–$CaCl_2$.

Exp. no.	Exp. condition Temperature / / Holding time	Oxygen conc. (mass ppm)		Nitrogen conc. (mass ppm)		Hv (kgf/mm^2)
		Initial	After exp.	Initial	After exp.	After exp.
3–C	1273K / 86ks	150	62	10	86	81.9
3–D		260	61	20	63	81.9
3–E		200	63	20	93	87.2
3–F		900	80	100	130	103
4–A	1323K / 79ks	110	86	5	63	90.1
4–E		200	100	20	75	93.5
5–A	1373K / 86ks	110	37	5	48	85.7
5–E		200	43	20	59	81.7
6–A	1423K / 40ks	110	94	5	53	90.2
6–E		200	72	20	82	87.6
7–A	1473K / 43ks	110	63	5	41	87.7
7–E		200	63	20 c	50	83.4
16–B1†	1273K / 90ks	130	27	10	51	89.2
16–B1†		130	28	10	43	–
16–B2†		130	34	10	65	–
16–E †		200	23	20	52	79.3
17–B1†	1273K / 90ks	130	16	10	41	85.0
17–B1†		130	17	10	34	–
17–E †		200	68	20	62	90.2
19–B1‡	1373K / 40ks	130	35	10	49	92.5
19–B1‡		130	22	10	45	–
19–B2‡		130	27	10	92	–
19–E ‡		–	–	–	–	89.9
24–B1¶	1273K / 86ks	130	500	10	53	125
24–B1¶		130	479	10	55	–
24–B2¶		130	482	10	83	–
24–E¶		200	474	20	77	114

†: Annealed at 1073K for 22ks

‡: Annealed at 1073K for 65ks

¶: Reacted under Ca–CaO equilibrium, and cooled in furnace.

For samples produced from the same starting material, their hardnesses increase with increasing oxygen concentration.

The dashed lines in Figure 3.4 are calculated from the data obtained by Okazaki and Conrad [7] on the assumption that the contribution of oxygen and nitrogen to the hardness of titanium solid solution are additive. The effect of grain size on hardness may be neglected because grain sizes of the deoxidized samples obtained in this study were more than 1mm. Considering the fact that the smallest hardness value measured by Okazaki and Conrad was 85 kg/mm^2 for titanium containing 135 mass ppm O and 100 mass ppm N, the values for the deoxidized samples containing about 50 mass ppm nitrogen in this study are somewhat larger than the calculated values based on above mentioned assumption. When the oxygen contribution to hardness was derived, it was based on the oxygen analysis only, and nitrogen and carbon pick–up during arc melting and heat were neglected [8]. It seems that the absolute values of hardness for titanium oxygen alloys, determined by them, include some uncertainty due to impurities other than oxygen especially for very dilute oxygen alloys.

Data lines extrapolated from Elssner *et al.*[9] and Baur and Lehr [10] are also plotted in Figure 3.4 for reference, however, they did not provide detailed information on grain size and nitrogen concentration. The scattering of the present data point in Figure 3.4 may be due to the contribution of impurities other than oxygen. No clear interrelation between minute metallic impurities and hardness was found.

3.3.3 Trace element analyses

Analytical values of trace impurity element levels in titanium before and after deoxidation are listed in Table 3.4. From the results of GDMS, it is notable that copper, silicon and nitrogen concentrations markedly increased after deoxidation. This is probably due to impurities in $CaCl_2$ which diffused into the titanium sample. As for chromium, nickel and calcium, the concentrations remained unchanged after the deoxidation treatment. The calcium concentration of the sample No.5–E was cross checked by using atomic absorption method; the analyzed values ranged from 0.8 to 1.2 mass ppm. The carbon concentrations in Table 3.4 are listed only for reference since the associated uncertainties are rather large because of the method of analysis.

Obinata *et al.*[4] reacted titanium powder with calcium in the temperature range,

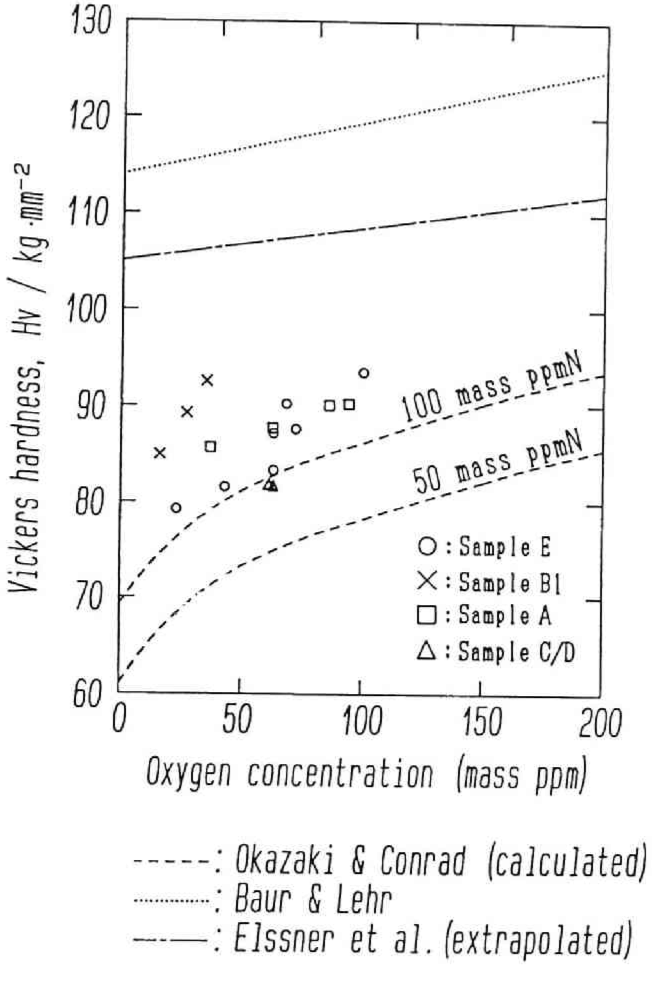

Figure 3.4: Effect of oxygen on the hardness of titanium. Micro Vickers hardness measurements (500g load) were performed on deoxidized titanium samples containing about 50 mass ppm nitrogen.

Table 3.4: Impurity concentrations of titanium samples. Metallic and carbon impurities were determined by glow discharge mass spectroscopy; oxygen and nitrogen by the method of inert gas fusion.

Sample No.	Conditions	Concentrations of impurities in tianium (mass ppm)									Note	
		O	N	C*	Cu	Si	Cr	Fe	Ni	Ca	RRR	Hv
A	(as received)	107	5	2.5	0.98	1.6	0.15	0.16	0.04	1.0	88.8	131
4-A	1323K-79ks	86	63	5.1	3.0	86	0.52	1.67	0.68	0.85	101	90.1
5-A	1373K-86ks	37	48	2.9	2.56	45	1.1	1.50	0.14	1.2	119	85.7
6-A	1423K-40ks	94	53	7.1	4.65	44	0.76	8.30	2.73	1.3	111	90.2
D	(as received)	260	20	1.4	0.38	0.69	0.19	0.19	0.04	1.5	21.1	116
3-D	1273K-86ks	61	63	10	1.9	24	0.28	0.59	0.07	1.1	122	81.9
C	(as received)	150	10	1.9	0.75	1.0	0.18	0.16	0.05	1.2	43.1	185
3-C	1273K-86ks	62	86	7.3	2.4	29	0.58	0.82	0.27	1.4	106	81.9
E	(as received)	200	20	5.0	0.90	3.1	13	8.94	15	1.4	-	105
5-E	1373K-86ks	43	59	5.9	3.4	48	15	10	14	1.1	-	81.7

* : include large uncertainity, listed for reference purposes only.

1118K to 1573K, and obtained the solubility of calcium in titanium. The calcium solubility they reported, which is about 60 mass ppm, is large compared with the data in Table 3.4. As there is no data about the diffusivity of calcium in titanium, it is difficult to discuss these differences at this stage.

3.3.4 Residual resistivity ratio measurement

In Table 3.5 typical measured values of electrical resistivity of titanium wires are listed as well as the results of oxygen concentration and Vickers hardness. The resistivity ratios, $\rho_{298}/\rho_{4.2}$(=RRR) and ρ_{298}/ρ_{77}, listed in Table 3.5 are fairly accurate since values do not include error associated with size measurements. Relationship between $\rho_{298}/\rho_{4.2}$(=RRR) and ρ_{298}/ρ_{77} for deoxidized samples were plotted in Figure 3.5. From the figure, it is shown that the value of $\rho_{298}/\rho_{4.2}$ for the sample can be estimated from the value of ρ_{298}/ρ_{77} especially for the sample with low value of $\rho_{298}/\rho_{4.2}$. The RRR values increased in all cases following deoxidation treatment; it is worth noting that the RRR value for electrolytically refined titanium wire reached a magnitude of hundred after deoxidation (e.g. No.4,5,6–A), while that for commercial grade titanium wire showed only about 17 (No.3–F).

In general, the resistivity of titanium at temperature T, ρ_T, can be put in the form

$$\rho_T = \rho_{i,T} + \rho_0 + \Delta_{T,C} \tag{3.3}$$

where $\rho_{i,T}$ is the "ideal resistivity" due to scattering of electrons by thermal vibration, ρ_0 is the residual resistivity at absolute zero (0 K) determined by impurities and lattice defects, and $\Delta_{T,C}$ is the deviation from Matthiessen's rule (DMR). The residual resistivity, ρ_0, is essentially equal to the resistivity at 4.2K, $\rho_{4.2}$, in the case of titanium because $\rho_{i,T} + \Delta_{T,C}$ is negligible compared to ρ_0 at 4.2K.

Assuming that Matthiessen's rule can be applied, that is, $\Delta_{T,C}$ in Equation (3.3) is zero, values measurable with a high degree of accuracy can be expressed as follows;

$$\frac{\rho_{77}}{\rho_{298}} = \frac{\rho_{i,77} + \rho_0}{\rho_{i,298} + \rho_0} \tag{3.4}$$

$$\frac{\rho_{4.2}}{\rho_{298}} = \frac{\rho_{i,4.2} + \rho_0}{\rho_{i,298} + \rho_0}. \tag{3.5}$$

Table 3.5: Results of resistivity measurements of deoxidized titanium wires. (Values in parentheses are estimated values.)

Sample no.	$\frac{\rho_{298}}{\rho_{4.2}}$	$\frac{\rho_{298}}{\rho_{77}}$	$\rho_{4.2}$	Oxygen conc.	Nitrogen conc.	Hv
	(=RRR)		(nΩm)	(mass ppm)		(kgf/mm^2)
B1 (as received)	26.8	7.52	17.0	130	10	224
16–B1	98.6	10.0	4.52	28	43	89.2
17–B1	97.5	9.92	4.58	17	34	85.0
19–B1	94.7	9.92	4.72	22	45	92.5
24–B1^b	27.3	7.78	17.1	500	53	125
B2 (as received)	24.4	7.39	19^a	130	10	–
16–B2	62.0	9.28	7.7^a	34	65	–
17–B2	(53)	9.12	(8.2)	(20)	–	–
19–B2	59.7	9.10	7.5^a	27	92	–
24–B2^b	23.9	7.48	20^a	482	83	–
A (as received)	88.8	9.60	4.9^a	110	5	131
4–A	101	9.90	4.5^a	86	63	90.1
5–A	119	10.2	3.9^a	37	48	85.7
6–A	111	10.1	4.1^a	94	53	90.2
C (as received)	43.1	8.54	11^a	150	10	185
3–C	122	10.1	3.6^a	62	86	81.9
3–D	106	9.82	4.1^a	61	63	81.9
F (as received)	9.28	5.10	54^a	900	100	201
3–F	17.1	6.85	27^a	80	100	103
24–F^b	11.5	5.74	42^a	(500)	–	132
F–anneal^c	(9.1)	5.09	(54)	990	90	154

a : Include large error due to size measurement.
b : Heat treated by using Ca–CaO equilibrium.
c : Annealed in silica tube at 1273K for 130ks.

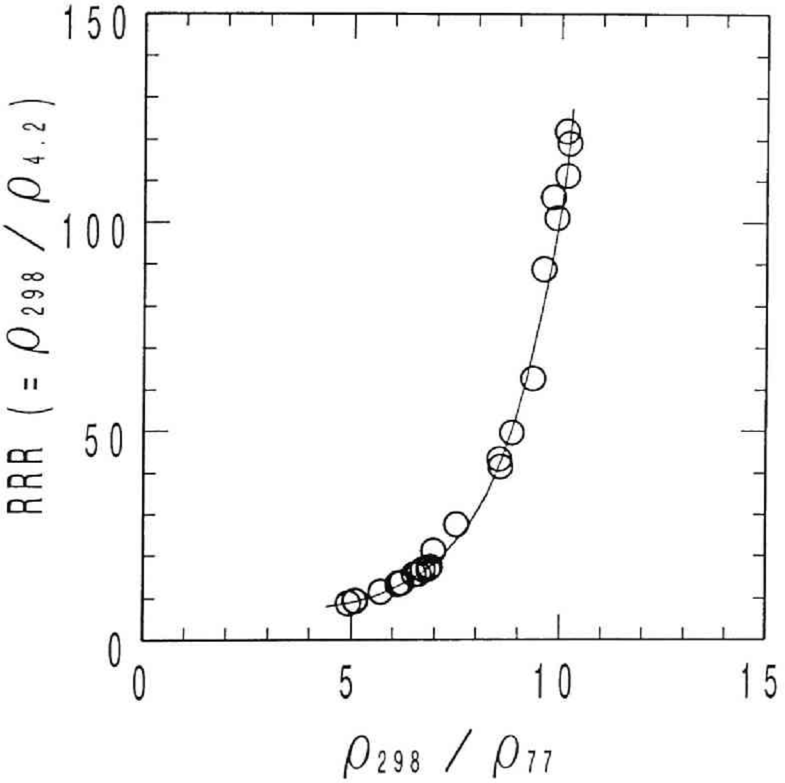

Figure 3.5: Relationship between $\rho_{298}/\rho_{4.2}$(=RRR) and ρ_{298}/ρ_{77} for deoxidized samples.

The relationship between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ can be obtained by eliminating ρ_0 from Equations (3.4) and (3.5) as follows,

$$\frac{\rho_{77}}{\rho_{298}} = A \cdot \frac{\rho_{4.2}}{\rho_{298}} + B \tag{3.6}$$

where A and B are $(\rho_{i,298}-\rho_{i,77})/(\rho_{i,298}-\rho_{i,4.2})$ and $(\rho_{i,77}-\rho_{i,4.2})/(\rho_{i,298}-\rho_{i,4.2})$, respectively. The values A and B in Equation (3.6) are constant, and independent of impurity concentration. Consequently, if Matthiessen's rule can be applied to titanium which contains dilute impurities, every pair of measured values (ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$) for the samples should fall on a straight line expressed by Equation (3.6), even though ρ_0 of these samples may be very large. Also the values, ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$, should approach the values, B and 0, respectively, as the purity of titanium increases (viz. ρ_0 approaches 0).

In Figure 3.6, measured values of ρ_{77}/ρ_{298} are plotted against $\rho_{4.2}/\rho_{298}$ for deoxidized titanium wires were plotted as well as for as–received titanium wires. The measured values for deoxidized samples fall a straight line but those for as–received titanium wires, especially for samples with high ρ_0 (high oxygen concentration), deviate from the straight line. This result indicates that the effect of oxygen on the term $\Delta_{T,C}$ in Equation (3.3) cannot be neglected, and that Matthiessen's rule cannot be applied to titanium with high oxygen concentration. From the 24 pairs of measured values for deoxidized titanium wires, the constants (Equation (3.6)), A and B were calculated using the least square approximation, and are depicted by the solid line in Figure 3.6.

$$\frac{\rho_{77}}{\rho_{298}} = 0.951 \cdot \frac{\rho_{4.2}}{\rho_{298}} + 0.0918 \tag{3.7}$$

The sum of A and B in Equation (3.6) should theoretically be one, whereas the measured value in Equation (3.6) is 1.04. This 4 percent discrepancy is somewhat large and cannot be attributed solely to experimental error, and seems to be due to DMR of samples with some impurities in addition to oxygen. That is to say, not only oxygen but also other impurities contribute to DMR for titanium to some extent. For a more rigid discussion concerning DMR, titanium purified further to a lower ρ_0 value is needed, and effect of hydrogen on resistivity must also be considered [12].

3.3.5 Influence of oxygen on electrical resistivity

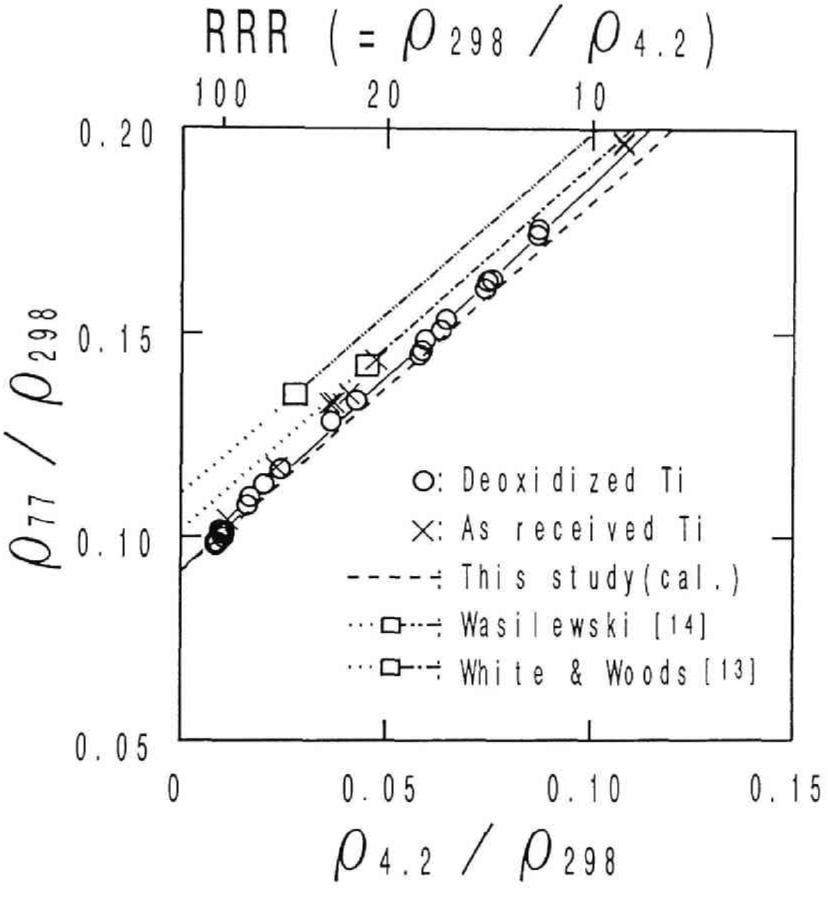

Figure 3.6: Relationship between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ for deoxidized titanium wires. The dashed line is calculated based on the results of deoxidized high purity titanium (RRR≃100) obtained in this study.

Table 3.6: Ideal resistivity of titanium at 298 and 77K.

	$\rho_{i,298}$ (nΩm)	$\rho_{i,77}$ (nΩm)	ρ_0 (nΩm)	Note
White & Woods [13]	437^a	44.5^b	19.7	$\rho_{i,273}$ = 390 nΩm
Wasilewski [14]	461^b	50.9	13.1	$\rho_{i,273}$ = 414 nΩm
G.Elssner *et al.* [9]	430			210 ppmO, 20 ppmN
This study	440	40	4.6	30 ppmO, 50 ppmN

a : Extrapolated.
b : Interpolated.

The residual resistivity, $\rho_{4.2}$, listed in the forth column of Table 3.5 most likely includes significant experimental error. All deoxidized wires were slightly etched by the salt and acid treatment, and except for sample B1, were too thin or short for accurate size measurement. The dimensions of sample B1, e.g. 80 mm in length by 1.8 mm in mean diameter, were measured fairly accurately unlike the other samples. The resistivity of this wire which includes a maximum error of 5% due to size measurements is, therefore, adopted in the following discussion.

In Table 3.6, the ideal resistivities at 77 and 298K were calculated by using sample Nos.16,17 and 19–B1 (see Table 3.5) on the assumption that $\Delta_{T,C}$ in Equation (3.3) is negligible for samples with RRR of about one hundred. The data obtained by White and Woods [13], Wasilewski [14] and Elssner *et al.* [9] are also listed for comparison. By using the values in Table 3.6, the constants A and B in Equation (3.6) can be calculated. Calculated relationships between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ are illustrated in Figure 3.6 along with their respective literature value (□). The dashed line in Figure 3.6 is calculated using the values in Table 3.6 obtained in this study. There is a large discrepancy between the three calculated lines, probably due to DMR. That is, in the calculation of $\rho_{i,T}$ in Equation (3.3) using a sample with large ρ_0, it is unavoidable that there is contribution of $\Delta_{T,C}$ to $\rho_{i,T}$. Therefore, it seems necessary to use as low residual resistivity as possible to minimize the interference by DMR in the determination of the ideal resistivity.

Table 3.7: Contribution of oxygen to the resistivity of titanium at several temperatures for various oxygen concentration ranges. ρ_T is the resistivity with lowest oxygen concentration at the measured temperature.

	$\Delta\rho/c$ (nΩm/mol%O)	T (K)	ρ_T (nΩm)	Oxygen conc. range (mol%O)
Ames & McQuillian [15]	113	293	470	— 1.5
Wasilewski [16]	123	273	427	0.13 — 10
Elssner *et al.*[9]	82	298	430	0.063 — 1.0
Komatsu *et al.*[17]	101	77	60.6	0.890 — 3.2
Baur & Lehr[10]	103	20.4	2.68	0.009 — 0.32
This study	88	4.2	4.60	0.009 — 0.15

The contribution by oxygen to the resistivity of titanium, $\Delta\rho$/c, determined in this study, as well as from the literatures, is given in Table 3.7 [9][10][15][16]–. The calculated value, 88 nΩm/mol%O, using the data for samples B1 in Table 3.5, which contained 28,17,22 and 500 mass ppm oxygen is in fairly good agreement with the reported data. It is noteworthy that values of $\Delta\rho$/c calculated from the data for samples B1 and F in Table 3.5 are 92 and 100 nΩm/mol%O, respectively, and that the residual resistivity increment associated with oxygen-doped samples, 24–B1 and 24–B2, from their respective deoxidized samples are almost the same amount.

As indicated by Aleksandrov [18], it is better to measure the resistivity at temperatures as low as possible in order to avoid introducing an additional error due to DMR to the desired $\Delta\rho$/c value. For this reason the value obtained in this study is believed reliable, but it should be noted that the range of oxygen concentrations in this study is rather limited, and the values themselves include some uncertainty.

3.4 Conclusions

Titanium in the form of wires and small pieces was deoxidized to a level of 20 – 60 mass ppm oxygen by use of Ca–$CaCl_2$ flux at 1273K. The micro Vickers hardness value of electrolytically refined titanium was 80–90 kg/mm^2 following deoxidation. The calcium, chromium, iron and nickel concentrations in titanium remained unchanged whereas impurities, such as nitrogen, copper and silicon, increased following deoxidation.

Resistivity measurements were carried out at 4.2, 77 and 298K on titanium wires. Deviation from Matthiessen's rule was observed for titanium samples even with high residual resistivity. By deoxidation of the electrolytically refined titanium wire, titanium with a high residual resistivity ratio ($\rho_{298}/\rho_{4.2} \simeq 100$) was produced, and the ideal resistivities at 77 and 298K were determined to be 40 and 440 nΩm, respectively. The contribution by oxygen to resistivity at 4.2K was also measured by using titanium samples containing 30 and 500 mass ppmO, and determined to be 88 nΩm/mol%O.

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Chapter 4

Electrochemical Deoxidation of Titanium

4.1 Introduction

In recent years, high–purity–titanium has found to applicable mainly as target material for semiconductor use [1][2]. The level of this titanium is between 99.999% and 99.9999%(excluding gaseous elements), with the major impurity being oxygen at about 0.01%(100 mass ppm). As the presence of oxygen in titanium leads to deterioration of titanium thin films[3], it seems important to produce lower oxygen titanium for semiconductor use. Furthermore, the development of an effective process for deoxidation of titanium could find application in the recovery of titanium scraps and in the production of low oxygen– containing titanium powders.

Oxygen removal directly from titanium–oxygen solid solution to a level below 100 mass ppm is very difficult because a large amount of oxygen dissolves in titanium to form an interstitial solid solution, and because titanium has a strong affinity for oxygen.

In recent years, some effective methods for removal of oxygen from titanium[4] and from titanium aluminide have been developed. In these previous chapters, deoxidation of solid titanium by reaction with a chemically active element, namely calcium–saturated $CaCl_2$ was examined in the temperature range 1273 to 1473K. The author succeeded in producing titanium containing less than 50 mass ppm oxygen with high residual resistivity ratio (RRR$\simeq$120) in the previous chapter. Calcium metal is thought to be the most effective deoxidation agent because it has an extremely strong affinity for oxygen, and because it scarcely dissolves in solid titanium. In the calcium–halide flux deoxidation process, the flux is used to contain the deoxidation agent calcium and, in addition, to facilitate the reaction by diluting the reaction product CaO, i.e., by decreasing the activity of the by-product CaO.

However, there exist limitations on the purity of flux and the initial oxygen content of the titanium used, since the ultimate limit of deoxidation is dependent on the amount of oxygen present as an impurity in the flux and on the amount of CaO produced during deoxidation.

In this chapter, the results of an experimental investigation directed towards the preparation of oxygen-free titanium by an electrochemical deoxidation method using $CaCl_2$ molten salt is reported. Hashimoto [5]–[7] proposed deoxidation of titanium during electro-winning of titanium metal using fluoride molten salt baths, but contamination of titanium by oxygen or carbon was encountered. In the present study, removal of O^{2-} (present as CaO in the flux) and production of calcium deoxidant by using an electrochemical technique are considered to improve the calcium–halide flux deoxidation process mentioned in the previous chapters. The behavior of other contaminants, such as carbon and nitrogen, is also discussed.

4.2 Principle

Since the principle of calcium–halide flux deoxidation of titanium has been reported in detail in the previous chapters, only a brief outline will be given here. Titanium–oxygen solid solution can be deoxidized by calcium by the following reaction:

$$\text{O (in Ti)} + \text{Ca (in flux)} = \text{CaO (in flux)} \qquad \frac{a_{CaO}}{a_O\, a_{Ca}} \tag{4.1}$$

The equilibrium oxygen concentration in titanium is thermodynamically decided by Equation (4.2) at temperature T.

$$[mass\%O] = \left(\frac{a_{\mathrm{CaO}}}{a_{\mathrm{Ca}}}\right)\left(\frac{1}{f_{\mathrm{O}}}\right)\exp\left(\frac{\Delta G^\circ}{RT}\right) \tag{4.2}$$

where ΔG° is the standard free energy change of the reaction of Equation (4.1), a_{CaO} and a_{Ca} are the activities of CaO and calcium, respectively, and f_{O} is the activity coefficient of oxygen in solid titanium.

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Ti-O 合金 O^{2-}

C/CO

The author determined oxygen potentials of β–titanium–oxygen solid solution at temperatures between 1173 and 1473K in chapter 1, and discussed the feasibility of preparation of low oxygen titanium by decreasing the activity of the by–product CaO using various calcium–halide fluxes in the presence of calcium metal. Several factors were considered in selecting a flux for deoxidation in chapter 3, and $CaCl_2$ was found to be the most desirable among many halide fluxes around 1300K, because CaO, the by–product of deoxidation, dissolves in $CaCl_2$ flux, and a lower limit of deoxidation is achieved by decreasing the activity of CaO (refer to Equation (4.2)). By submerging titanium in the form of wire and small pieces in calcium–saturated $CaCl_2$, the titanium samples were deoxidized to a level of 50 mass ppm. There exist, however, limitations on the purity of flux and the initial oxygen content of the titanium used, since the ultimate limit of deoxidation depends on the final oxygen concentration in the flux, as mentioned before.

The modified calcium–halide flux deoxidation method, examined in this chapter, is characterized by both production of calcium from the $CaCl_2$ flux and by effective removal of O^{2-} (present as CaO in the flux) dissolved in the flux by means of an electrochemical technique as expressed schematically in Figure 4.1. In this method, as expressed by Equation (4.3), cathode titanium is deoxidized by calcium which is produced electrochemically on the surface of the cathode according to Equation (4.4). O^{2-} species in the flux are continuously carried to the carbon anode, and oxygen in the flux is removed from the system as CO (or CO_2) gas by the anodic reaction expressed by Equation (4.5).

$$\begin{aligned} \text{O (in Ti)} + \text{Ca (in flux)} &= \text{Ca}^{2+}\text{ (in flux)} + \text{O}^{2-}\text{ (in flux)} && (4.3)\\ \text{Ca}^{2+}\text{ (in flux)} + 2\text{e}^- &= \text{Ca (on Ti cathode : in flux)} && (4.4)\\ \text{O}^{2-}\text{ (in flux)} + \text{C (carbon anode)} &= \text{CO (gas)} + 2\text{e}^- && (4.5) \end{aligned}$$

Unlike the calcium–halide flux deoxidation process examined in previous chapters, it is not necessary to add metallic calcium as a deoxidant since the activity of calcium near the cathode can be increased by controlling the applied voltage between the titanium cathode and carbon anode. In some cases, calcium can even be precipitated on the cathode by using an applied voltage more than the theoretical decomposition voltage of $CaCl_2$ (3.25V at 1223K). This electrochemical method has another advantage in that elimination of impurities originating from metallic calcium deoxidant, is not a concern.

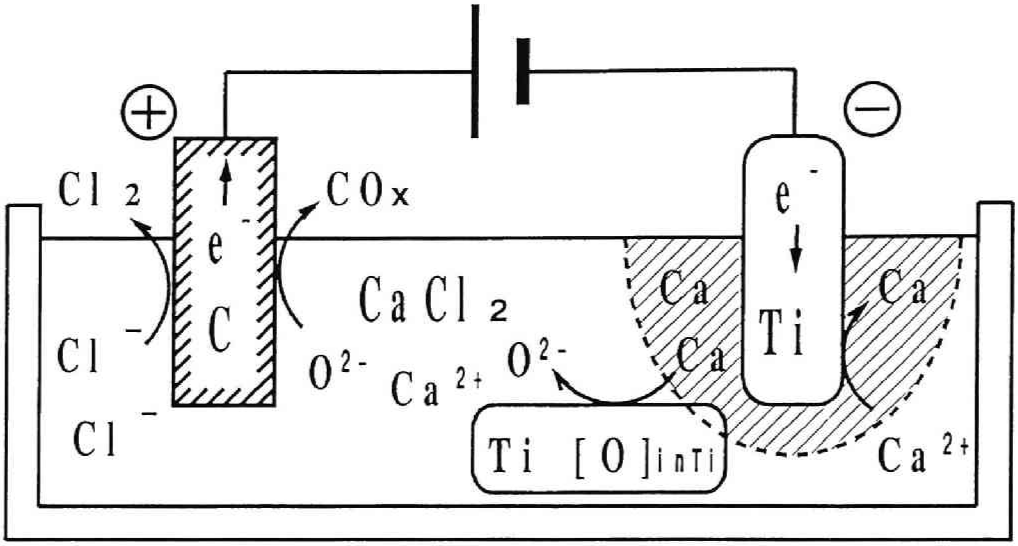

Figure 4.1: Principle of deoxidation of titanium by an electrochemical technique.

Table 4.1: Titanium samples used for deoxidation experiments.

Sample	Grade[a]	Oxygen conc. (mass ppm)	Nitrogen conc. (mass ppm)	Carbon conc. (mass ppm)	Configuration
A[b]	99.9999	140	<10	20	2.9 mmϕ wire
B[c]	99.99	200	20	<10	0.1g small pieces
C[d]	99.9	800	60	30	1.5 mmϕ wire
D[d]	99	900	20-50	30-50	1 mmϕ wire
E[d]	99.9	1400	20	50	2 mmϕ wire

a : Excluding gaseous elements.
b : Electrolytically refined sponge, followed by electron beam melting.
c : Electron beam melted high purity sponge.
d : Commercial grade titanium.

4.3 Experimental

4.3.1 Starting materials

As shown in Table 4.1, titanium of various forms, small pieces and wires [9], with different oxygen concentrations and configurations were used as starting materials. $CaCl_2$ used in this study was reagent grade anhydrous $CaCl_2$ (99.9%) in powder form, dried at 800K for more than 200ks(2 days).

4.3.2 Experimental procedures

A schematic illustration of the apparatus is shown in Figure 4.2. $CaCl_2$ flux which

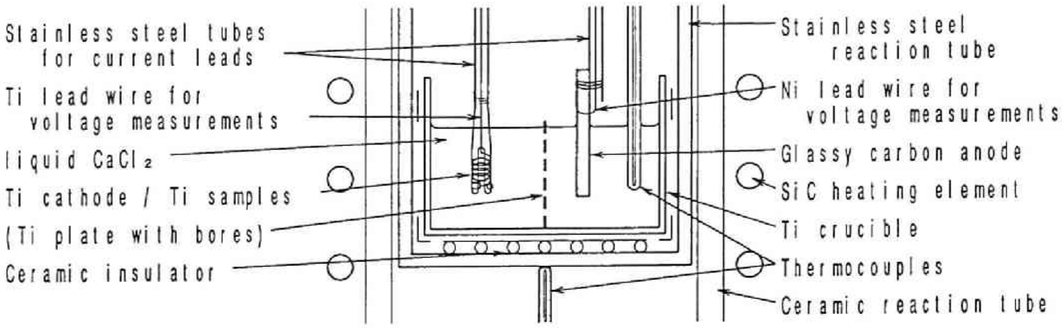

Figure 4.2: Schematic illustration of the reaction cell.

had been dehydrated beforehand was contained in a titanium crucible(72mm–dia., 160mm–height) and set in a stainless steel reaction tube. The titanium cathode was comprised of several strands of titanium wire samples about 50mm long. The total electrode surface area was approximately $1000mm^2$. High purity(99.9%) glassy carbon was used as an anode (100mm–length, 5.9mm–dia.). These electrodes as well as thermocouple tubing were inserted into the reaction tube through a gas tight water cooled stainless steel head.

After the assembled cell was evacuated at about 600K to ensure a completely gas–tightness and moisture–free system, argon was introduced into the reaction tube. The furnace was then heated to 1223K. After melting of $CaCl_2$, the glassy carbon anode was inserted into the molten salt, and pre–electrolysis was conducted. About 1.5V was applied between the titanium crucible and the carbon anode for about 2ks, for the purpose of eliminating residual gaseous impurities in the molten salt. The temperature of the molten salt was directly measured using a chromel–alumel thermocouple protected by a nickel sheath. After the pre–electrolysis, the titanium cathode was inserted into the molten $CaCl_2$, and a deoxidation experiment was carried out by applying voltages between 0 and 6V between the electrodes, which were separated by a distance of about 30mm.

In most cases, deoxidation of the titanium cathode, consisting of titanium samples with various oxygen concentrations, was effected by applying a voltage over 2.5V at 1223K for longer than 18ks(5 hours). To minimize carbon contamination, a titanium plate (1mm–thick) with many bored holes (4.5mm–dia.) was put between the cathode and anode to divide the crucible into two compartments. In some experiments, titanium samples were contained in a titanium cup(15mm–dia./24mm–height) or covered with titanium foil(0.1mm–thickness), and fastened to the cathode.

After reaction, the electrodes were pulled out from the molten $CaCl_2$, and the cell was allowed to cool in a stream of argon gas. In some cases, only the titanium cathode was replaced after cooling, for the next experimental run. The fused salt which adhered on the surface of the titanium electrode was removed by leaching with (1+1) acetic acid, and then the titanium samples of the electrode were carefully cleaned in (1+10) warm aqueous HCl solution followed by water, alcohol and acetone, and then allowed to dry.

4.3.3 Analysis

The titanium samples obtained were subjected to oxygen, nitrogen and carbon analyses using LECO analyzers. Preceding the analyses, samples were surface etched with a 1:4:10 mixture of $HF–HNO_3–H_2O$. For the purpose of increasing the accuracy of the oxygen and nitrogen analyses, 1g of platinum foil containing $4.4\pm1.0\mu$g oxygen and $0.2\pm0.2\mu$g nitrogen was used as an extraction bath for each 0.1g titanium sample. One of the representative analytical values of oxygen and nitrogen analysis used for calibration of the analyzer were listed for reference in Table 4.2. From the table, it is noted that the detection limit of oxygen in titanium (0.1g) by using platinum extraction bath is 10 mass ppm because fluctuation of oxygen amount in platinum was about 1μg. In some analyses, a 1g nickel bath containing $20\pm5\mu$g oxygen was employed. The instrument for oxygen analysis was calibrated by using iron standard samples containing 127±5 mass ppm oxygen, and the measured values were cross checked with titanium standard samples (440 and 1540 mass ppmO). In Table 4.3, representative analytical values of oxygen and nitrogen analysis of titanium samples were listed for reference. The data listed in Table 4.3 were calibrated using the data obtained in Table 4.2.

Trace metal analysis in titanium was carried out using glow discharge mass spectroscopy (GD–MS) by two companies specialized in the technique.

4.4 Results

4.4.1 Observation of the reaction

In cases where the applied voltage was less than 2V, the current between the electrodes was about 0.01A or less, and a calm molten salt surface was observed from the view port of the stainless steel head. The current increased sharply when the applied voltage exceeded 2.5V, and was 0.2– 0.5A at 3V and about 2A at 3.3V. When the applied voltage was more than 3.3V, fuming in the vicinity of the anode was observed. This gas evolution may result from the decomposition of $CaCl_2$ as the theoretical decomposition voltage of $CaCl_2$ is 3.25V at 1223K [8].

4.4.2 Relationship between reaction time and oxygen concentration

Figure 4.3 shows the relationship between reaction time and oxygen concentration of titanium samples. These data were obtained by analyzing more than 50 samples at applied voltages of more than 3.3V. This series of experiments was conducted to determine whether deoxidation could be effected, and to determine the amount of time necessary for the reaction. Various kinds of titanium samples (listed in Table 4.1) containing 1400, 900, 800 and 200 mass ppm oxygen were deoxidized to a level below 100 ppm after reaction at 1223K for more than 21ks. It is noteworthy that the plotted values below 100 mass ppm in Figure 4.3 include some uncertainty because most of these samples were analyzed using the nickel extraction bath.

In the following experiments, the deoxidation reaction was conducted at 1223K for more than 21ks, and the platinum extraction bath was used for oxygen analysis to increase the analytical accuracy.

4.4.3 Oxygen, nitrogen and carbon analysis

Table 4.2: Representative analytical values of oxygen and nitrogen analysis used for calibration of the analyzer. The obtained values were calibrated by using iron standard samples (Fe–ss: 0.0127±0.0005 mass%O, 0.0078±0.0003 mass%N) and blank values of platinum extraction bath containing 4.4μgO/g and 0.2μgN/g.

Sample no. & code	Sample weight (g)	Before calibration (μg)		After calibration (mass ppm)	
		Oxygen	Nitrogen	Oxygen	Nitrogen
Fe-ss-322	0.9997	137.6	78.5	132	78
Fe-ss-323	0.9973	131.5	78.8	127	78
Fe-ss-324	0.9963	130.2	78.7	126	78
Fe-ss-357	1.0006	127.8	79.3	123	78
average(4)	0.9984	131.7	78.8	127	78
Pt-332	(1)[a]	5.8	0.4	1	0
Pt-333	(1)[a]	3.6	0.1	-1	0
Pt-334	(1)[a]	4.1	0.4	0	0
Pt-335	(1)[a]	4.1	0.1	0	0
Pt-351	(1)[a]	4.7	0.2	0	0
Pt-360	(1)[a]	4.2	0	0	0
average(6)	(1)[a]	4.4[b]	0.2[b]	0	0

a: Platinum extraction bath about 1.00+-0.05g were assumed to weigh 1g.

b: Mean absolute amount of oxygen and nitrogen contained in platinum extraction bath were used as calibration factor.

Table 4.3: Representative analytical values of oxygen and nitrogen in titanium samples obtained in one analytical run. The data were calibrated using the calibration factor obtained in Table 4.2. To ascertain reliability of the calibration, titanium standard samples (ss-1540: 0.154±0.003 mass%O, 0.018±0.004 mass%N, ss-440: 0.044±0.003 mass%O, 0.004±0.002 mass%N) were analyzed.

Sample no. & code	Sample weight (g)	Before calibration (μg)		After calibration (mass ppm)	
		Oxygen	Nitrogen	Oxygen	Nitrogen
ss-1540-336*	0.1083	181.1	25.9	1569	235
ss-1540-337*	0.1081	178.6	26.0	1549	236
ss-1540-338*	0.1075	175.3	25.6	1529	233
ss-440-339*	0.1069	56.3	1.6	466	13
Raw-n+	0.1036	19.2	0.2	136	0
Raw-f+	0.1354	197.8	14.3	1374	103
No.46-f-low#	0.1281	12.8	1.5	62	10
No.46-n#	0.1076	15.4	0.9	97	6
No.46-n-nallow#	0.0764	11.3	1.6	84	19
No.46-n-non-W#	0.1151	14.9	0.5	86	3
No.46-s#	0.0805	10.2	3.9	67	46
No.47-f#	0.1057	12.7	2.2	74	19
No.47-n(f)#	0.1059	13.7	1.9	83	16
No.47-s#	0.0727	8.9	3.7	58	48
No.49-f#	0.1189	5.9	2.3	11	17
No.49-s#	0.0796	4.7	3.7	1	43

* : Titanium standard samples.

+ : Starting materials.

\# : Deoxidized samples.

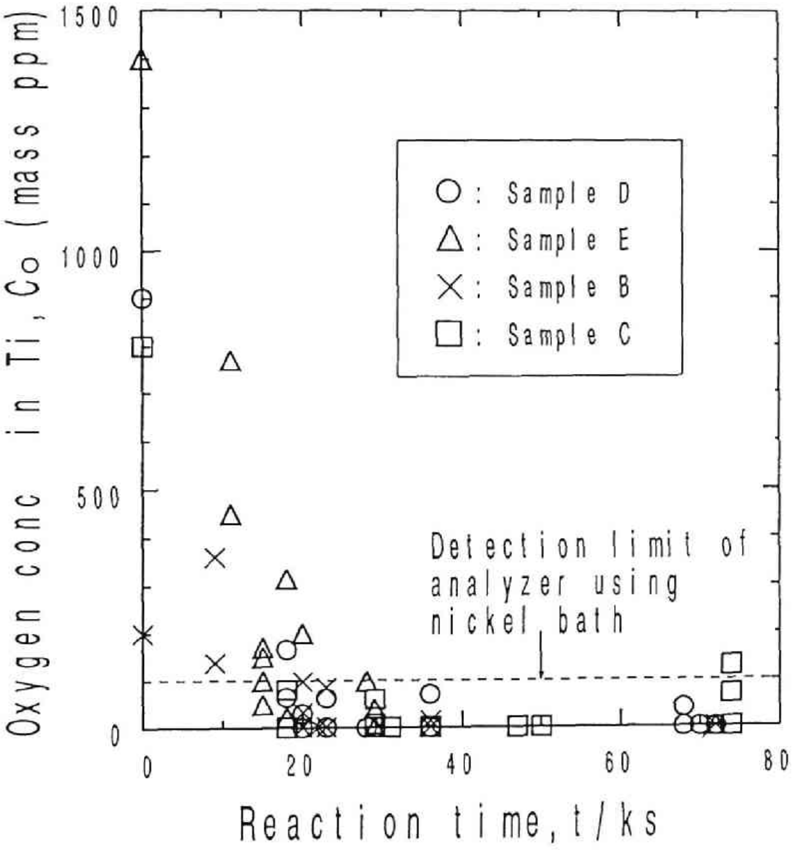

Figure 4.3: Relationship between reaction time and oxygen concentration in titanium samples.

Some representative analytical results for the oxygen, nitrogen and carbon concentrations in titanium before and after experiments are listed in Table 4.4. As indicated by the results of Exp. nos. 49 and 53, titanium samples could be deoxidized to below the limit of detection by applying voltages of more than 3.4V, however, the carbon concentration is increased to about 900 mass ppm.

By inserting a titanium plate with many bored holes between the cathode and anode, carbon contamination of the titanium samples was depressed, as shown by Exp. no. 17 in Table 4.4. Either titanium samples wrapped in titanium foil (Exp. no.51), did not experience a marked increase in carbon concentration, but effect of deoxidation became worse.

When the applied voltage between the electrodes was decreased to about 2.8 to 3.0V, carbon pickup was depressed to some extent, as shown by Exp. nos. 46, 47, 44 and 21 in Table 4.4. Under these experimental conditions, some titanium samples containing less than 100 mass ppm oxygen and carbon were obtained.

Nitrogen concentrations in the samples were, in most cases, independent of the experimental conditions, and did not change after deoxidation treatment.

4.4.4 Effect of applied voltage on carbon dissolution into titanium

The results in Table 4.4, suggest that the dissolution of carbon into titanium can be reduced by decreasing the applied voltage between electrodes. Therefore, the influence of applied voltage on carbon concentration was examined at 1223K for 22ks in the voltage range, 0 to 3.7V. The results are summarized in Figure 4.4. All of the titanium electrodes used in this experiment were made from the same starting material (Sample D in Table 4.1) in the same configuration. Figure 4.4 indicates that deoxidation is effected by applying a voltage of more than 2.5V. On the other hand, the carbon concentration is increased markedly when a voltage of more than 3V is applied. In the case of no applied voltage, the titanium sample picked up oxygen from the bath, and the oxygen level increased from 900 to 980 mass ppm.

The nitrogen concentrations of the samples were the same before and after experiments, also in this study.

4.4.5 Analysis of trace metal elements by GD–MS

Table 4.4: Experimental details and analyses of titanium samples before and after deoxidation.

Exp. no.	Experimental conditions	Impurity concentration in titanium (mass ppm)						
		Oxygen		Nitrogen		Carbon		
		Init.	After exp.	Init.	After exp.	Init.	After exp.	note
49	1223K / 22ks	900	<10	40	40	30	900	
	3.5V / 1.8A	1400	<10	20	20	50	670	
53	1223K / 22ks	900	<10	50	50	30	870	
	3.4V / 2.1A	1400	20	20	50	50	1000	
17	1173K / 23ks	900	60	20	20	30	60	Ti plate used
	4.0V / 1.8A							
46	1223K / 22ks	140	100	<10	<10	20	20	
	3.0V / 0.27A	900	70	50	50	50	220	
		1400	60	20	20	50	50	
47	1223K / 22ks	140	80	<10	20	20	130	
	3.0V / 0.35A	1400	70	20	20	50	150	
51	1223K /22ks	900	90	50	100	50	440	
	2.9V / 0.50A	900	770	20	30	30	60	in Ti foil
44	1223K / 22ks	900	50	40	40	50	60	
	2.8V / 0.50A							
21	1173K/ 27ks	900	<10	20	20	30	30	
	2.8V / 0.40A	1400	100	20	50	50	70	

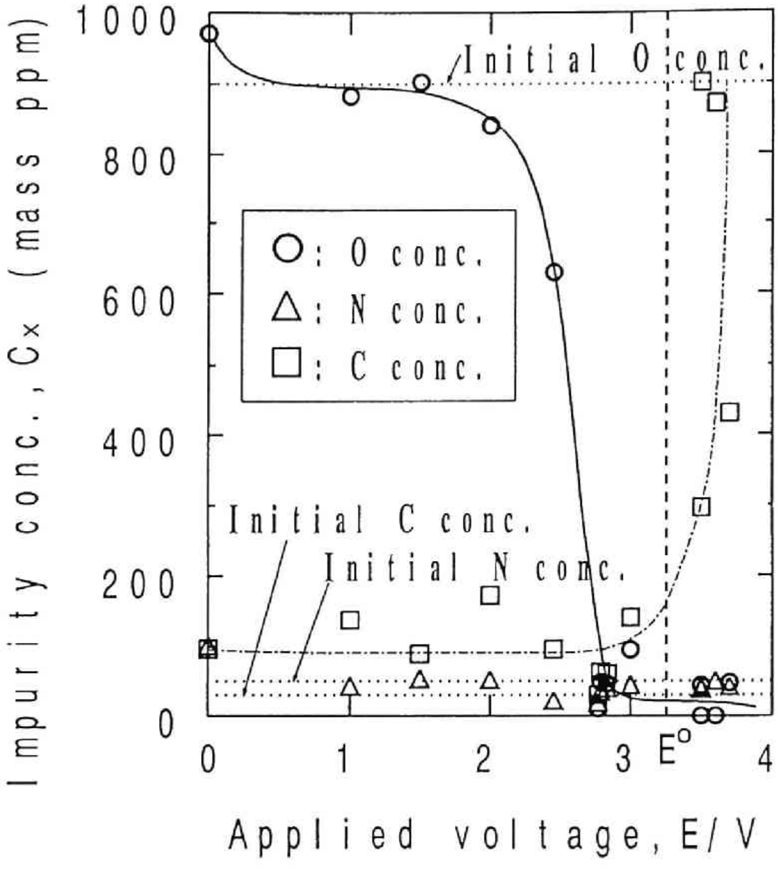

Figure 4.4: Effect of applied voltage on the oxygen, nitrogen and carbon concentrations in titanium after reaction.

Results of trace metal analysis by glow discharge mass spectroscopy (GD–MS) are listed in Table 4.5. To monitor the behavior of impurities, electrolytically-refined high purity titanium [9](Sample A in Table 4.1) was used. The titanium wires obtained after deoxidation were divided into some pieces, and sent to different companies for analysis. The results of GD–MS show that the levels of metallic impurities other than nickel, iron and chromium remained almost unchanged after the deoxidation treatment. After the reaction, iron and chromium concentrations increased slightly, and the level of nickel increased markedly to about 30 and 2 mass ppm in Exp. nos. 46 and 47, respectively, from an initial concentration of less than 0.1 mass ppm. These increments are probably due to contaminants arising from the stainless steel used in the cell assemblies, and the large increment in nickel concentration of Exp. no. 46 in Table 4.5 may be attributed to the nickel tubing which was submerged in the molten salt for temperature measurement.

4.5 Discussion

4.5.1 Deoxidation reaction

Previously reported results of the calcium–halide flux deoxidation process and the deoxidation reaction (Equation (4.1) or Equation (4.3)) given in this paper indicate that oxygen removal proceeds when the activity of calcium is increased and/or the activity of CaO in contact with titanium samples is decreased. Since titanium was deoxidized to a level below 10 mass ppm in this study, it is clear that the electrochemical technique decreases the activity of CaO more effectively than the calcium–halide flux deoxidation process reported previously.

In the experiment in which more than 3.3V was applied between the electrodes, deoxidation seems to be promoted by calcium metal precipitated near the titanium surface, resulting from the decomposition of $CaCl_2$. In this case, the activity of calcium would be unity, and therefore, the deoxidation limit would be decided by the activity of CaO in $CaCl_2$. Thus, deoxidation is greatly facilitated by the large drop in CaO activity, because the decomposition voltage of CaO is much lower than that of $CaCl_2$.

The observation that deoxidation is promoted by applying a voltage between

Table 4.5: Analytical results of deoxidized titanium samples by glow discharge mass spectrometry(GD-MS).

Exp. no.	Impurity concentration (mass ppm)											Analyzer[a]
Exp. conditions	Ca	Na	Mg	Ni	Fe	Cr	Al	Si	Cu	U	Th	
Starting material	1	-	-	0.04	0.2	0.1	0.1	0.9	0.8	-	-	X
	0.98	0.12	<0.01	0.03	0.13	0.14	0.18	1.2	0.67	<0.1	<0.1	Y
	-	<0.02[b]	-	<0.1[b]	0.15[b]	0.1[b]	0.1[b]	-	0.8[b]	<0.0005[c]	<0.0005[c]	Z
No. 46 /1223K-3.0V-0.27A-22ks	1	-	-	27	1	0.3	0.1	1	2	-	-	X
	0.77	0.06	<0.01	29	0.37	0.16	0.16	0.94	1.1	<0.1	<0.1	Y
No. 47 /1223K-3.0V-0.35A-22ks	1	-	-	2	2	1	0.2	1	1	-	-	X
	0.91	0.04	<0.01	1.4	0.21	0.15	0.16	0.76	0.76	<0.1	<0.1	Y

a : Samples were analyzed by different companies.

b : Analyzed by flameless atomic absorption spectrometry (FL-AAS).

c : Analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

2.5 and 3.0V, which is below the decomposition voltage of $CaCl_2$, indicates that considerable deoxidation takes place without precipitation of calcium metal. This reaction is probably promoted by decreasing CaO activity (or O^{2-}), accompanied by increasing calcium activity near the titanium sample. The decomposition of CaO (refer to Equation (4.5)) occurs around 1.5V when the activity of CaO in $CaCl_2$ is not low. But, under the present experimental condition, the reaction of Equation (4.5) may occur at a much higher voltage because the activity of CaO is very low. The result that deoxidation was effected by applying a voltage of more than 2.5V, as shown in Figure 4.4, is probably due to this decomposition of CaO.

4.5.2 Contamination by carbon

Hashimoto [5][6] indicated that calcium precipitated on a cathode would dissolve in the salt and diffuse to the carbon anode to react with carbon as shown by Equation (4.6), during the electro-winning of titanium metal using fluoride molten salt bath.

$$\text{Ca (in flux)} + \text{C (carbon anode)} = \text{CaC}_2 \text{ (in flux)} \tag{4.6}$$

Calcium-carbide(CaC_2) formed on the anode would again dissolve in $CaCl_2$, and this CaC_2 would act as a carbon donor to the titanium samples. As reported solubilities of calcium and CaC_2 in $CaCl_2$ are about 0.15mol% [10] and 12mol% [11] at 1223K, respectively, it is possible that these types of reactions occurred in the present investigation. However, the presence of CaC_2 in $CaCl_2$ could not be confirmed by both X-ray diffractometry and X-ray microprobe analysis.

It is clearly shown, though, that the carbon concentration in titanium increases sharply with voltage at values greater than the decomposition voltage of $CaCl_2$, as seen in Fig.3. This behavior may be explained by the fact that carbon concentration in the form of CaC_2 in $CaCl_2$ was increased by the precipitation of calcium, namely, increase in calcium activity. When the applied voltage was between 2.5 and 3.0V, the carbon concentration in the vicinity of the titanium cathode was probably very low and thus carbon concentration in the titanium samples did not increase so much (Exp. nos. 44 and 21 in Table 4.4) after 22ks.

4.6 Conclusions

Removal of oxygen in titanium using an electrochemical technique was examined at temperatures around 1223K. It was supposed that calcium activity is increased and CaO activity is decreased around the titanium cathode surface by applying voltages between titanium and carbon electrodes immersed in molten $CaCl_2$, and that these activity changes proceed the deoxidation of the titanium cathode samples.

Titanium wires containing 1400 mass ppm oxygen were deoxidized to less than 100 mass ppm by applying more than 2.5V between titanium and carbon electrodes, and, in some cases, the oxygen concentration in titanium was lowered to below the detection limit($<$ 10 mass ppm) of conventional inert gas fusion analysis, whereas the carbon concentration was increased from 20∼50 to 50∼70 mass ppm.

The effect of applied voltage on oxygen, nitrogen and carbon concentrations in titanium was also investigated, and 2.8V was found to be the optimum for deoxidation.

In the production of oxygen–free–titanium, the behavior of metallic contaminants was investigated using electrolytically refined high–purity–titanium as starting material. Calcium, aluminum, silicon and copper concentrations in titanium remained unchanged whereas the nickel, iron and chromium concentrations increased by 1 to 2 mass ppm.

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Chapter 5

Preparation of Titanium Powders by Calciothermic Reduction of Oxides

5.1 Introduction

Titanium is expensive for producing and subsequent forming. Consequently, a lot of efforts have been expended to reduce the cost of titanium parts. The major thrust in cost reduction has been to produce near–net shape parts, which has led to much research and development of powder metallurgy (P/M) techniques[1]. The P/M techniques are useful to produce the near–net–shape parts which leads to greater cost reduction than the combination of milling, machining and welding. However, most of the cost for P/M is comprised of the cost of starting material powders. The titanium and its alloy powders are produced by atomizing titanium produced by Kroll or Hunter process. Mechanically crushed titanium sponge under 100 mesh is generally termed "sponge fines", and its major impurities are oxygen and chlorine at levels of a few thousands mass ppm, respectively. Chlorine level must be below at least 100 mass ppm to avoid deterioration of the quality, therefore, once melted titanium starting stock is generally comminuted to produce chlorine free powders. Two methods that are currently used for powder production are mechanical comminution of the starting stock, such as hydride–dehydride(HDH) process, and plasma rotating electrode process (PREP). Purity of these powders are between 99 and 99.9% excluding gaseous element where the major impurity is oxygen ranging from 500 to 5000 mass ppm.

For the sake of simplicity of the process, titanium reduction directly from its oxide has been attempted, and much efforts have been made to reduce titanium oxide by utilizing strong affinity of calcium for oxygen[2][3]. This calciothermic reduction process is characterized by starting from easily available oxides, but there are some difficulties[4] relating to removal of oxygen to the level satisfying the commercial standards. One of the important advantages of this process is easy to produce very fine powders at relatively low temperatures in a short reaction period.

So far the direct compound reduction techniques have been successfully used for the preparation of permanent magnetic materials, such as Sm–Co[5]–[7] and Nd–Fe–B [8]–[12], and the superconducting Nb_3Sn powders[13]. The obtained reduction product was very fine powder in general, since calciothermic reduction of oxides produces solid metals at relatively low temperatures without melting. The chemical reactions to produce titanium powders from oxides can be described by the equation:

$$TiO_2 + 2\ Ca = Ti + 2\ CaO \tag{5.1}$$

Calcium hydride(CaH_2) may also be useful for the reduction of TiO_2 because of its strong affinity with oxygen[12][14]–[16]. This reducing agent has been used to produce Sm–Co and Nd–Fe–B magnets by the co-reduction or Reduction–Diffusion process[7][11].

In this part, the usefulness of the calciothermic reduction for producing fine and pure titanium powders is discussed. From the view point of commercial use, this study mainly deals with oxygen content and morphology of the titanium powders.

5.2 Experimental

5.2.1 Materials

High purity TiO_2 powders(99.8%) were used in this study: the particle size was of the order of sub-microns. Both calcium and CaH_2 used were of about 89% purity, in which CaO and water were main impurities. Anhydrous calcium-chloride ($CaCl_2$) used as flux had a purity of 99.9%.

5.2.2 Experimental procedures

Figure 5.1 represents the procedures of this work. The main procedures for preparation of titanium powders by calciothermic reduction consists of three steps; (1) blending of the starting material; (2) high–temperature reaction; and (3) acid leaching for removal of by–products. The apparatus and experimental method for these experiments are similar to those described in the previous chapters. The reduction experiments were carried out in a stainless steel vessel as shown in Figure 5.2.

The premixed raw material powders (4g of TiO_2, 6g of CaH_2) were mainly used. In the case of reduction by calcium metal, 4g of TiO_2 powder was mixed with 6g of calcium granules. In some cases, CaO powder was added to the mixtures to prevent sintering of the produced titanium powders.

In the experiments using $CaCl_2$ flux, two types of starting material were prepared. In one case, 2.4g of TiO_2 powder was mixed with 3.6g of calcium granules and 20g of $CaCl_2$ powder. In the other case 2.0g of TiO_2, 4.0g of CaH_2 and 8g of $CaCl_2$ were blended.

Taking account of leakage of the vapor from the reaction vessel, the charged amount of the reductant was 1.3 to 2.0 times more than the stoichiometric amount necessary for the reduction. In this calculation, the stoichiometric amount of CaH_2 was calculated by assuming that hydrogen gas does not contribute to the oxide reduction.

These mixtures were compacted and placed on the molybdenum dish in the vessel as shown in Figure 5.2, and heated in the furnace. Special care was taken to avoid the leakage of the reductant from the vessel.

After a given holding time in the purified argon atmosphere at a reduction temperature between 1123K and 1373K, in most cases at 1273K, the vessel was cooled in a furnace.

The reduction products containing the desired titanium powder, CaO and the residual reducing agent often formed a hard cake. They were pulverized into fine powders, and mixed with water. The slurry is then put in aqueous CH_3COOH solution (pH=3) with supersonic vibration or stirring. The centrifuged compound powders were rinsed with distilled water, alcohol and acetone, then dried in a vacuum.

Electron–beam (EB) melting was made by compacting the obtained titanium

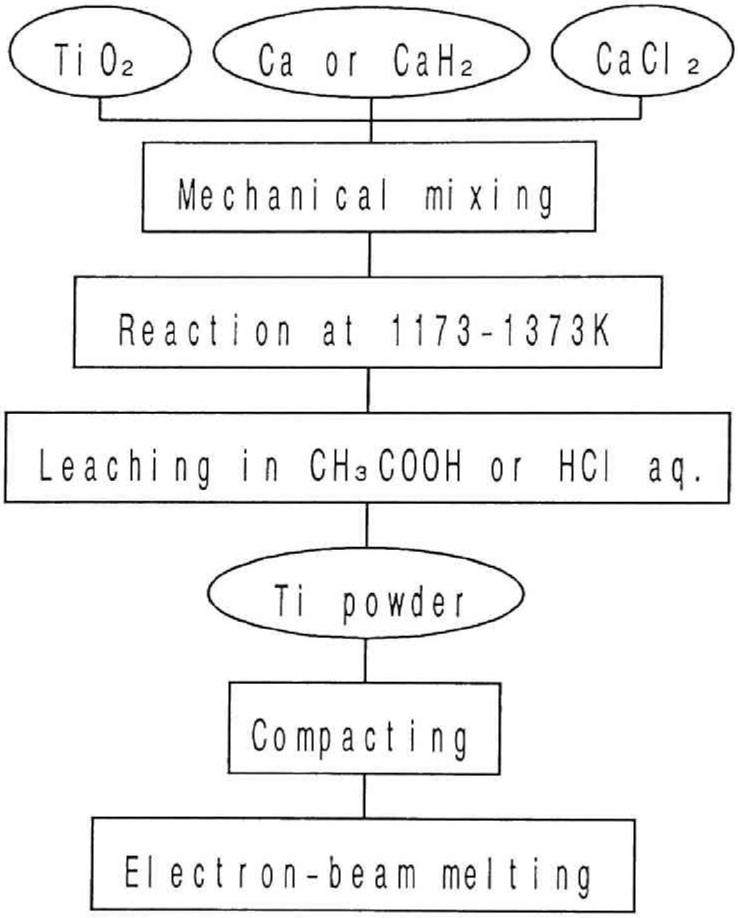

Figure 5.1: Experimental procedures for calciothermic reduction of titanium oxides.

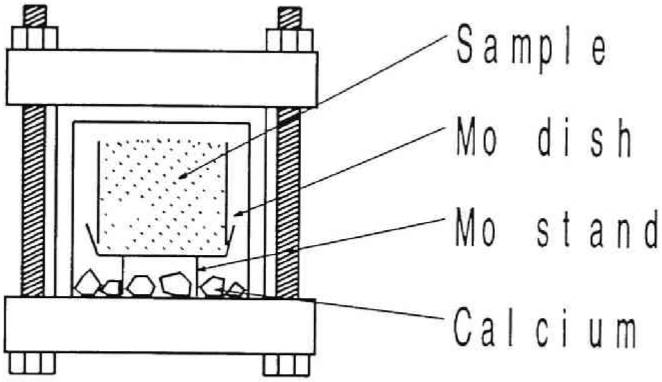

Figure 5.2: Reaction vessel arrangement.

powders in the form of pellet. The pellet was pre–heated in vacuum in the EB furnace before melting in order to avoid dispersion due to thermal shock and rapid liberation of adsorbed gas, and then melted to eliminate residual CaO in the powder.

5.2.3 Analysis

The identification of the phases existing in the specimens was carried out by X–ray diffractometry using a Philips PW1700 system, and the results were compared with JCPDS cards. X–ray microprobe analysis (XMA, Hitachi X–650) was done to obtain the compositional profiles. The morphology and configuration of the powder were examined by scanning electron microscopy (SEM, Hitachi S–450). A LECO TC–336 analyzer was used for oxygen analysis of the samples, and calcium was chemically analyzed by atomic absorption spectrometry (SIMADZU AA–670).

5.3 Results and Discussion

5.3.1 Reduction of TiO_2 by using calcium metal

After the reduction by calcium, the obtained hard cake was made of the mixture of titanium metal, residual calcium and by-product CaO, and it was difficult to pulverize mechanically. Titanium powders were sintered into coralloidal form which were filled with calcium and it oxides. This agglomeration into a hard mass caused slow rate of reaction with acid, and prevented from an effective leaching to obtain highly pure titanium powders. The oxygen concentration of the obtained titanium powders after leaching was scattered between 2000 and 4000 mass ppm. By adding CaO powder to the starting mixtures to prevent the titanium powders from sintering, average oxygen concentration of the powders were lowered to some extent and the reproducibility of analytical values was improved, whereas the titanium powders containing oxygen below 2000 mass ppm were scarcely but obtained.

Suzuki *et al.* reported that oxygen concentrations in titanium powders scattered largely between 2000 and 7000 ppm[17] in the case of the reduction of TiO_2 by calcium vapor. The result obtained in this study is consistent with the data reported by Suzuki *et al.*

5.3.2 Ability of CaH_2 as a reductant

To demonstrate feasibility of reduction of TiO_2 by CaH_2, titanium wires were reacted with CaH_2 in the reaction vessel at 1273K for 80ks. As shown in Table 5.1, several kinds of titanium wires containing different amounts of oxygen were deoxidized to the level of several hundreds mass ppm, therefore, CaH_2 can be used as reductant to reduce TiO_2 to this oxygen level. These results agreed well with those obtained in the equilibrium experiments described in chapter 1. After the reduction of TiO_2 by CaH_2, CaH_2 was hardly detected by X-ray diffraction measurements, while the metallic calcium was found in the mixture. This result indicates that CaH_2 dissociated into calcium and hydrogen gas below 1273K, as seen from the thermodynamic calculation[18].

According to Borok[15], the dissociation of CaH_2 and evolution of hydrogen begins at 673K, and TiO_2 could be reduced at 1423K. Based on these data, TiO_2 may be reduced by calcium vapor or liquid which is produced by decomposition of CaH_2 at the reduction temperature in this study. Fine CaH_2 powder is commercially available, and it is easier to mix with TiO_2 powder than calcium granules, therefore,

Table 5.1: Deoxidation of titanium wires and small pieces by CaH_2 at 1273K for 173ks.

Oxygen concentration (mass ppm)	
Berfore deoxidation	After deoxidation
2800	530
2570	550
2000	650
2000	680
1960	430
1670	440
1400	620
1400	430

CaH_2 powders may produce wider contact area with the oxide particles than calcium granules, and seems to be effective for reduction.

5.3.3 Reduction of TiO_2 by CaH_2

The obtained cake after the reduction by CaH_2 was porous and easy to crush mechanically. CaO and calcium existed in the cake were easily removed by the subsequent wet method. After the leaching, X-ray diffraction measurements confirmed that no phases except pure titanium existed in all the specimens in this experimental conditions.

The scanning electron micrographs in Figure 5.3 revealed the morphology of the calciothermic titanium powders. The fine titanium particles which is lightly sintered to form coralloidal morphology could be seen after the removal of CaO. The particle size was found to depend significantly on the reducing time. The reduced powders were found to have a tendency to be sintered at higher temperatures or for longer periods of reaction.

Change in oxygen, nitrogen and calcium contents of the powders with reduction time is shown in Figure 5.4. Titanium powder produced after 58ks reduction by CaH_2 (see Figure 5.3:(C)) contained about 1500 mass ppm oxygen. Analytical values for nitrogen include some uncertainties because nitrogen gas extraction during analysis seemed to take place incompletely from the nickel–tin bath. Therefore, these values were plotted only for reference. The lowest oxygen concentration of the powder produced in this experimental condition was about 900 mass ppm, although the theoretical deoxidation limit of titanium by calcium at 1273K is 500 ppm as mentioned in chapter 1. This 400 mass ppm difference is probably due to oxygen or oxygen compounds such as CaO adsorbed on the surface or trapped in the concave of the particles.

Figure 5.4 shows that considerable amount of calcium was remained in the powder after the rinsing. As mentioned in chapter 2, calcium hardly dissolves in titanium[19], therefore the analyzed calcium seems to be physisorped calcium or CaO which could not be removed by rinsing. By the improvement of rinsing, the titanium powders containing 280 mass ppm of calcium were obtained.

Figures 5.3 and 5.4 show that the oxygen concentration in the reduced titanium powders depends on the particle size. The more sintered powders contain less oxygen whereas calcium contents are almost constant. This probably means that the

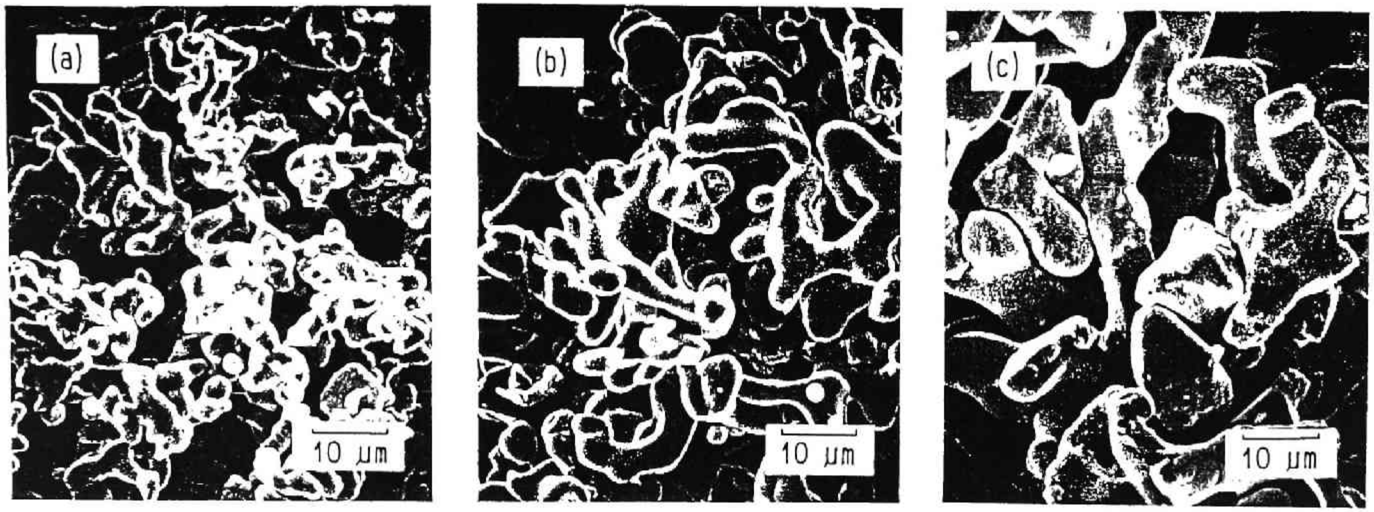

Figure 5.3: Scanning electron micrographs of titanium powders reduced by CaH_2 at 1273K for (a): 3.6ks, (b): 21.6ks and (c)57.6ks. Calcium and CaO was removed by leaching before observation. The oxygen concentration of these powders were analyzed to be (a): 3400 ppm, (b): 2100 ppm and (c): 1500 ppm.

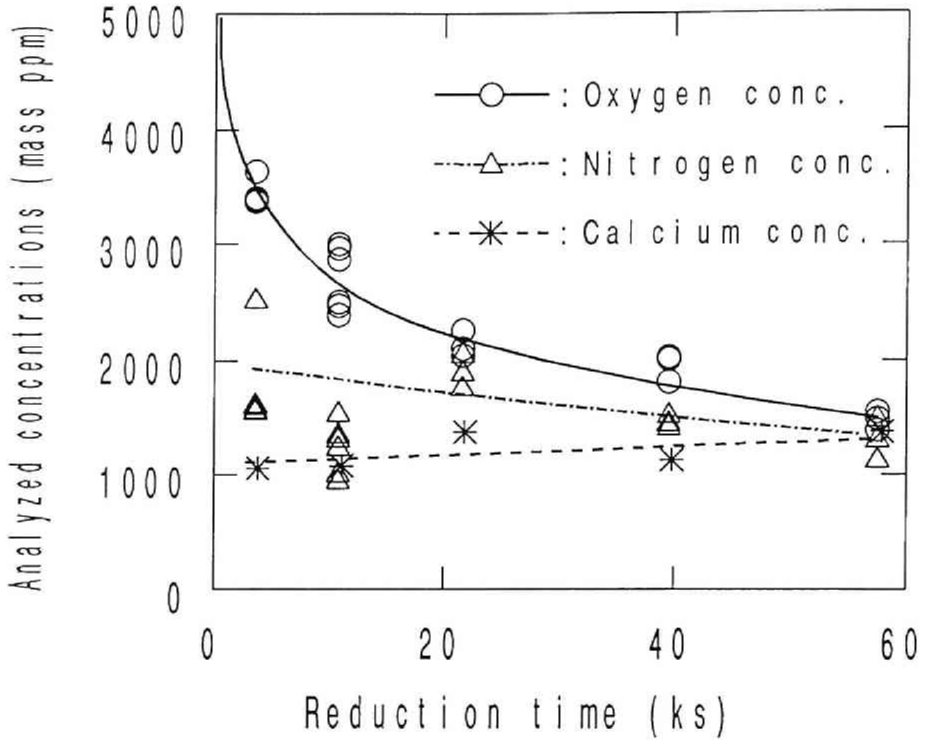

Figure 5.4: Change in oxygen, nitrogen and calcium concentration of the titanium powders with holding time of the reduction. The powders were obtained by reduction of TiO_2 powders at 1273K using CaH_2 and subsequent leaching by aqueous CH_3COOH solution.

oxygen concentration in the powder is considerably affected by the re–oxidation of the surface of the fine particles during handling in air and acid after the reduction.

5.3.4 Reduction of TiO_2 by using Ca–$CaCl_2$ flux

The use of $CaCl_2$ as flux gave better results in average oxygen concentration in titanium powder than the reduction without flux. Fine titanium powders were obtained after the reduction at 1273K by using either CaH_2 or calcium as a reductant as shown in Figure 5.5. XMA analysis did not detect any traces of chlorine or CaO in the powders after leaching, and these powders contained about 1100 mass ppm oxygen. The reproducibility of analytical values of oxygen concentrations in the powder produced in this condition was highest among the conditions tested in this study.

5.3.5 Results of reduction and deoxidation by using various reductants

Results of oxygen analysis after the reduction of TiO_2 were summarized in Table 5.2 as well as the results after the deoxidation of titanium small pieces or wires, which were obtained in the previous chapters. The oxygen levels in the reduced powders were higher than that in the deoxidized titanium metals. This may be caused by the difference of the particle size and morphology. Fine powders obtained by reduction of TiO_2 are easily contaminated by the trapped impurities on the irregular surface, therefore, difference of oxygen concentrations between reduced powders and deoxidized bulks in the same experimental condition seems to be reasonable.

5.3.6 Electron–beam melting of the powders

Sectioned EB melted titanium button is shown in Figure 5.6. The starting titanium powder was obtained by reducing TiO_2 using CaH_2. Figure 5.6 shows that the CaO particles were concentrated to form a precipitate during electron–beam melting. In Figure 5.6 (a), segregation of CaO in titanium bulk can be observed in a section of the EB melted titanium. Residual CaO in the reduced powders seems to be agglomerated into the round inclusions. Figure 5.6 (b) is the extended scanning electron image of the boundary between the segregated CaO inclusions and

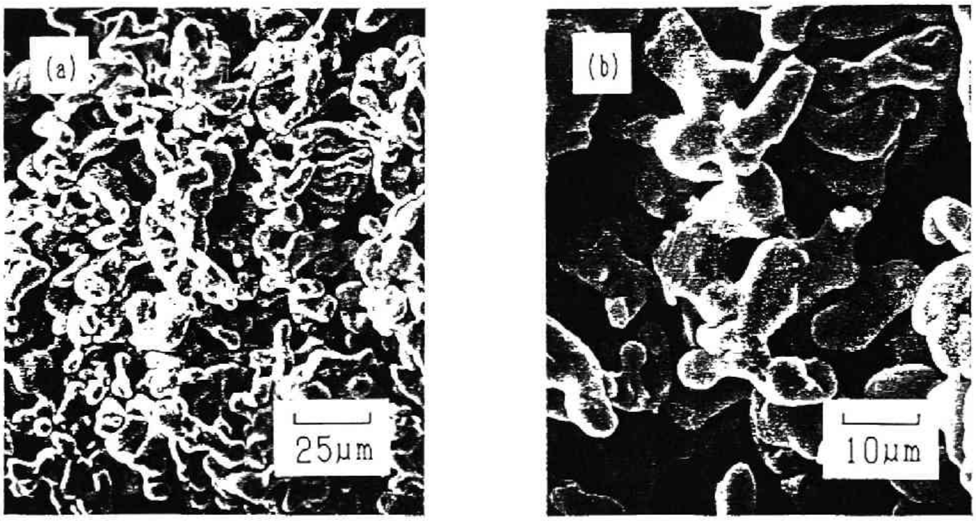

Figure 5.5: Scanning electron micrographs of titanium powders reduced by calcium using $CaCl_2$ flux at 1273K for 43.2ks. CaO and the flux were removed by leaching before observation. Photograph (b) is a magnified image of a part of photograph (a). The oxygen concentration of the powder was analyzed to be 1100 mass ppm.

Table 5.2: Comparison of the final oxygen concentration of titanium powders reduced from TiO_2 powders with those of deoxidized titanium wires using various reductants.

Reductants	Oxygen concentration (mass ppm)			
	Deoxidized from Ti metal		Reduced from TiO_2	
Calcium	450	550	2000	4000
CaH_2	400	700	900	1500
Calcium + $CaCl_2$	30	200	700	1500

EB melted titanium bulk, and Figure 5.6 (c) is the characteristic X–ray image of Ca$K\alpha$ part corresponding to Figure 5.6 (b). This CaO inclusions show the reduced powders contained a small amount of CaO and/or calcium even after the leaching. Electron beam melting might be used for the elimination of calcium in the reduced titanium.

5.4 Conclusions

The clean and fine titanium powders were produced directly from the TiO_2 powders by the calciothermic reduction at 1273K using calcium granules or CaH_2 powders. By using CaH_2 as a reductant, the titanium powders containing about 1500 mass ppm oxygen were obtained after the removal of residual calcium and by–product CaO by leaching. The use of $CaCl_2$ flux gave better results on the oxygen concentrations in the reduced powders, and titanium powders containing about 1100 mass ppm were produced.

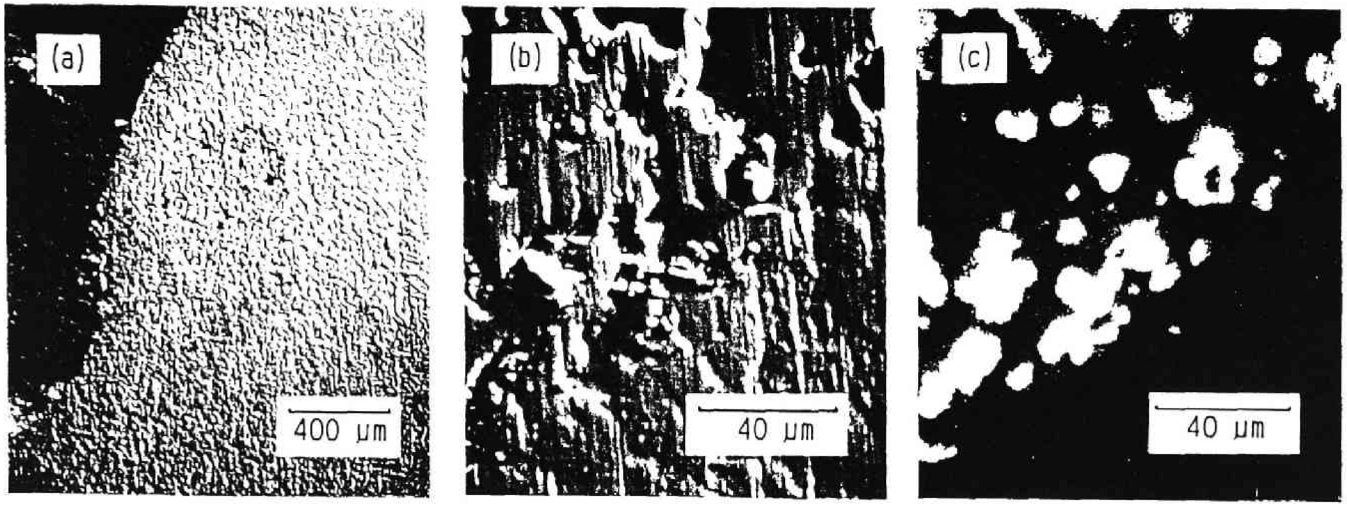

Figure 5.6: Photographs showing the segregated CaO inclusion which were concentrated during EB melting of the titanium powders obtained by the calciothermic reduction – acid leaching process.

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Part III

Refining of Titanium Aluminides

Chapter 1

Thermodynamic Study on the Ti–Al–Ca System at 1273K

1.1 Introduction

Study on refining of titanium aluminides with the scope of developing effective process to produce clean and fine titanium aluminide powders were carried out in this part, because there has been considerable interest in developing titanium aluminides as a structural material.

In the previous part, a fundamental study on calcium halide flux deoxidation of pure titanium to produce extra-low-oxygen titanium, and calciothermic reduction of titanium oxide to produce low oxygen fine titanium powder were carried out. By employing findings and knowledge acquired in the previous part, investigation of direct deoxidation of titanium aluminides powders by using calcium–aluminum alloy was carried out. Furthermore, the direct compound reduction techniques, called the co-reduction process or reduction diffusion (RD) process, were also applied for production of low oxygen titanium aluminide powders directly from oxides.

At first glance, the deoxidation of titanium aluminides presents some difficulties. Pure calcium, which is effective in the reduction of titanium oxide and the deoxidation of titanium, seems to be inadequate for the deoxidation of titanium aluminides because of the strong affinity between calcium and aluminum which results in Ca–Al alloy formation. For example, TiAl allowed to react with pure calcium or a Ca–Al alloy of lower aluminum activity than TiAl will undergo aluminum depletion at the surface and form aluminum-poor compounds or alloys, such as Ti_3Al, at the interface as shown schematically in Figure 1.1 (a) . On the other hand, the reaction between TiAl and Ca–Al alloy of higher aluminum activity than that in TiAl will result in diffusion of aluminum from Ca–Al alloy to TiAl and formation of aluminum–rich compounds (e.g. $TiAl_2$, $TiAl_3$) at the surface as shown in Figure 1.1 (c). Therefore, knowledge of the phase equilibria existing between TiAl and Ca–Al alloys is essential for selection of a suitable Ca–Al alloy deoxidant or reductant.

Prior to the calciothermic deoxidation experiment, phase equilibria in the Ti–Al–Ca system at the reaction temperatures were investigated to determine Ca–Al alloy compositions in equilibrium with titanium aluminides. As shown in the binary phase diagrams of the system Ti–Al, Ca–Al and Ca–Ti in Figures 1.2, 1.3 and 1.4, titanium and calcium are mutually insoluble whereas aluminum has strong affinity both with titanium and calcium. As there is no literatures concerning phase relation in the Ti–Al–Ca ternary system, Ca–Al alloy compositions in equilibrium with titanium aluminides were determined in this chapter. This information of the phase relation is utilized for developing an effective process to produce high purity titanium aluminide powders in a desired composition by calcium halide flux deoxidation of titanium aluminide powders and calciothermic reduction of oxides.

1.2 Experimental

The laboratory investigation of the phase equilibria existing between TiAl and Ca–Al alloys was comprised of two types of experimental procedures — one was diffusion coupling of the two materials at 1273K, and the other, isothermal annealing of metal powder mixtures of the Ti–Al–Ca system at 1273K. The apparatus and experimental method used for these experiments were similar to those described in the previous part.

1.2.1 Diffusion couple experiment

Diffusion couple experiment was conducted in order to identify the compositions of Ca–Al alloy in equilibrium with TiAl. The small pieces of 99%–pure TiAl or powders (produced by plasma rotating electrode process) were used. 99.5%–pure aluminum powder (200 mesh) and 98%–pure calcium granules (about 3mm dia.) was mixed in various compositions (0 to 67mol%Al), and in some cases pre–alloyed

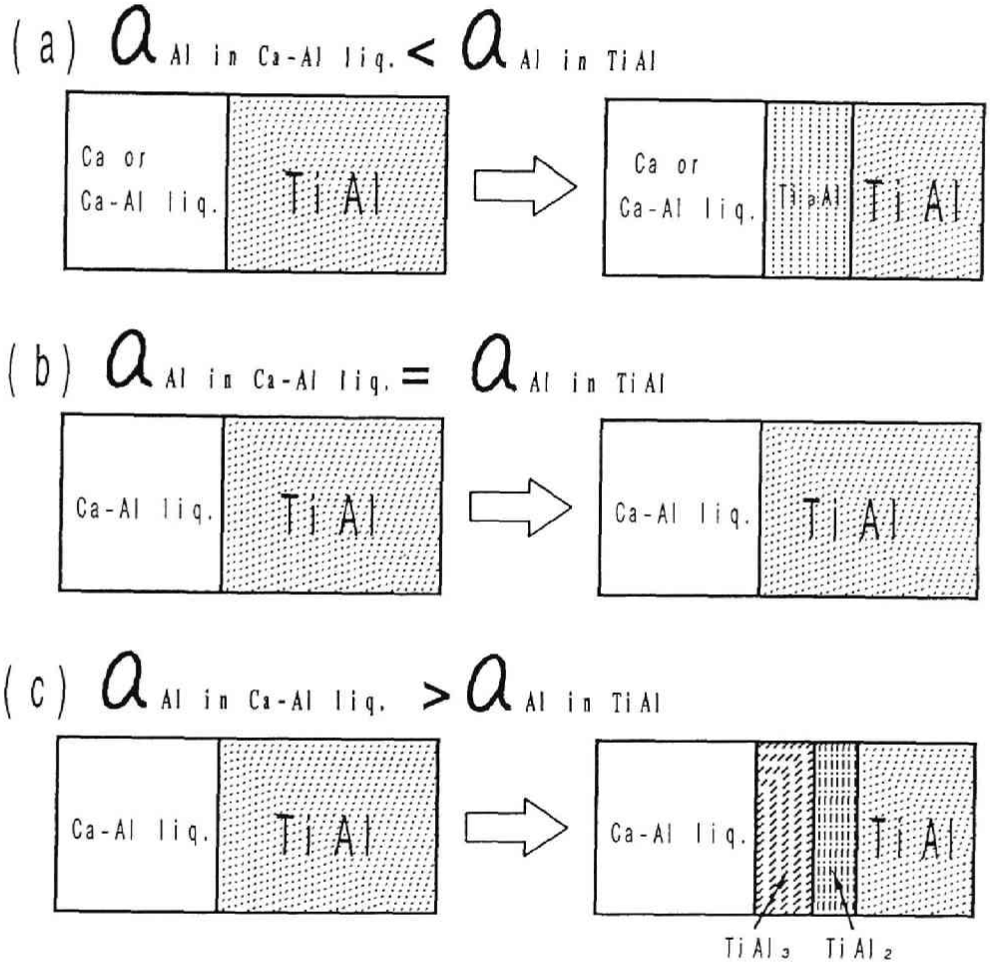


Figure 1.1: Reaction between TiAl and Ca–Al alloys with various aluminum activities.

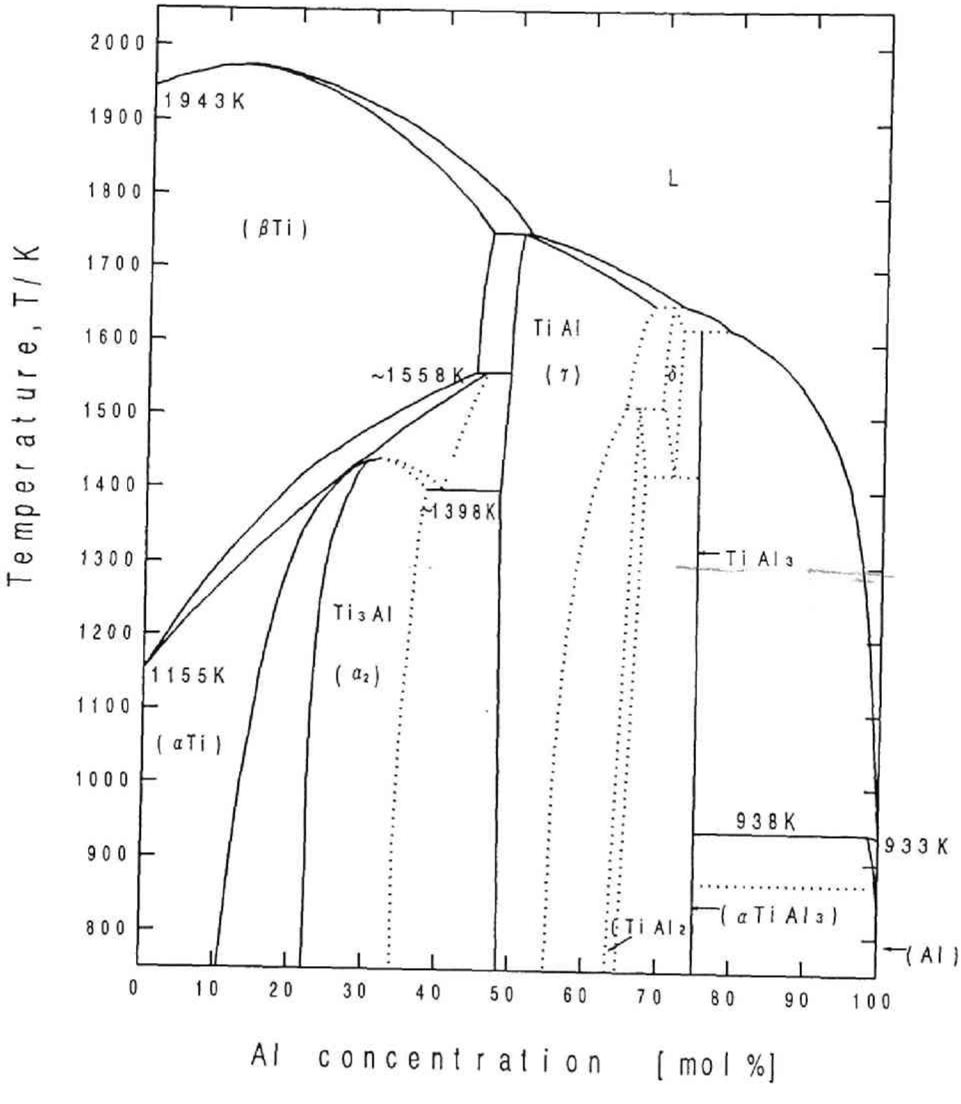


Figure 1.2: Phase diagram of the Ti–Al system[1].

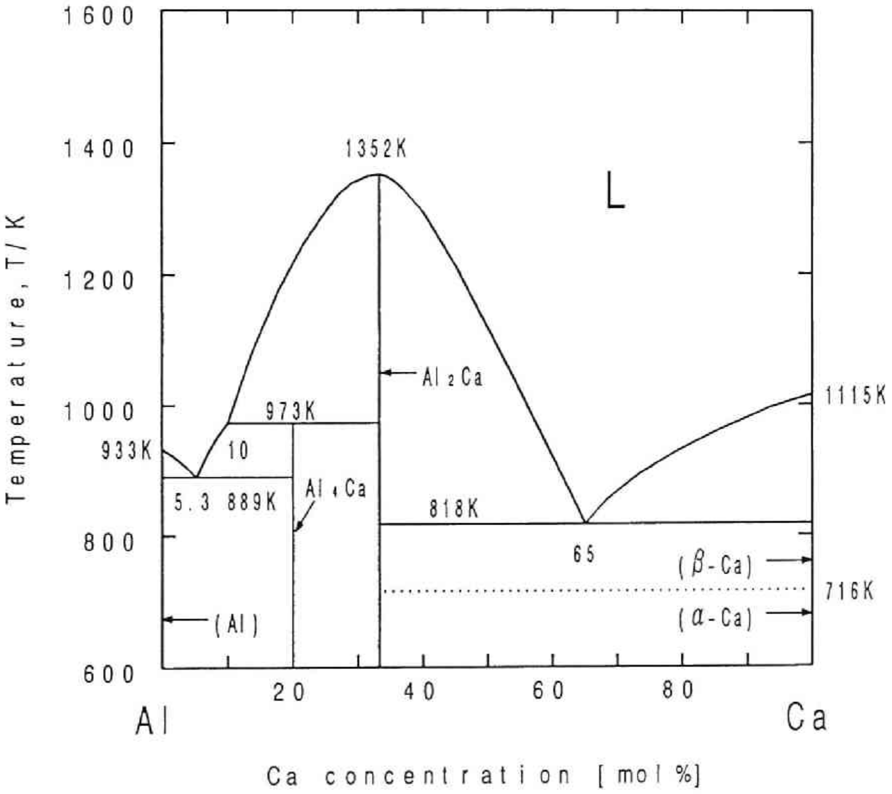


Figure 1.3: Phase diagram of the Ca–Al system[2].

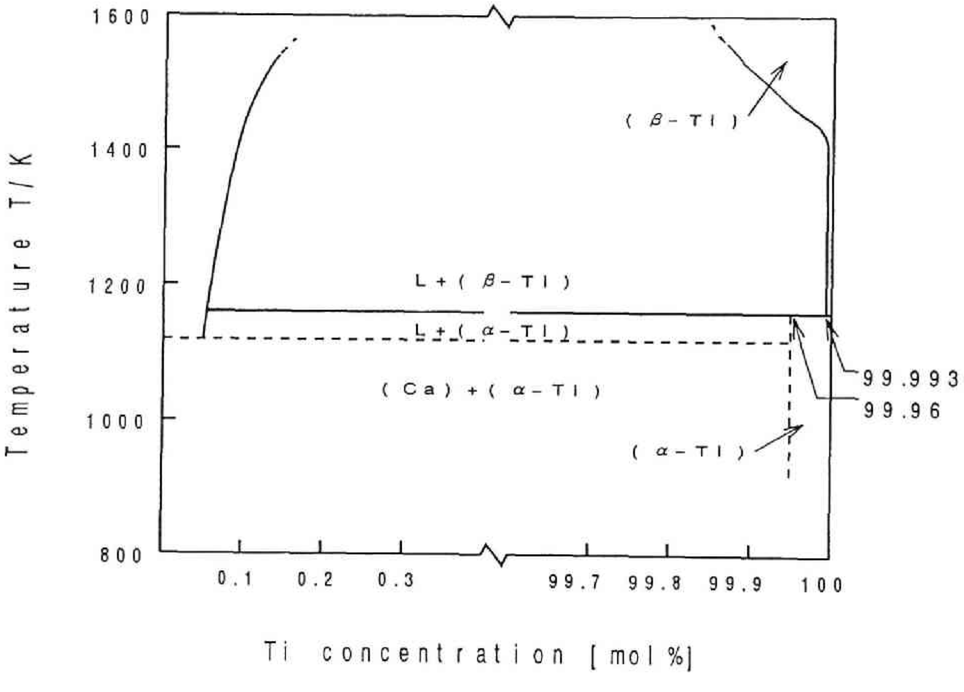


Figure 1.4: Phase diagram of the Ti–Ca system[3].

Ca–Al was also used. TiAl samples, calcium granules and aluminum powder were placed in a molybdenum crucible which was inserted into a stainless steel tube, and then sealed at both ends by welding in an argon gas atmosphere, as shown in Figure 1.5. The assembled tube was heated in an electric furnace to a temperature of 1273K, and the holding time was 86.4ks. Afterwards, the reaction tube was removed from the furnace and quenched in water. The samples, TiAl small pieces and/or powders, were subjected to phase and composition analyses.

1.2.2 Isothermal annealing experiment

In addition to the diffusion couple experiment, isothermal annealing of metal powder mixtures of various initial compositions was performed to verify the phase equilibria results. This experiment was carried out to scrutinize the phase equilibria of the Ti–Al–Ca system in various compositions at 1273K. The starting materials consisted of 99%–pure titanium powder(200 mesh), 99.5%–pure aluminum powder (200 mesh) and 98%–pure calcium granules (about 3mm dia.). Samples of various compositions were prepared by thorough mixing of starting materials to the desired ratios using an agate mortar and pestle. 10–gram sample mixture placed in a molybdenum crucible was sealed in a stainless steel tube, and was heated to a temperature of 1273K. The holding time was between 73ks and 1Ms. Afterwards, the reaction tube was quenched in water. The samples obtained, which consisted of mixtures of titanium, aluminum and calcium, were subjected to phase analysis.

1.2.3 Analysis

Aluminum and calcium were chemically analyzed by inductively coupled plasma–atomic emission spectrometry (ICP–AES, Nippon Jarrell–Ash ICAP–575II). To ascertain the accuracy of the analyzed values, titanium and calcium analysis was performed independently by a company by an electrothermal atomizer (flameless) atomic absorption spectrometric method.

Identification of the existing phases in the sample was carried out by powder X–ray diffractometry (XRD) using a Philips PW1700 system, and the results were compared with JCPDS cards and the reported data of Al_2Ti[4]. X–ray microprobe analysis (XMA, Hitachi X–650) was done to obtain the compositional profiles.

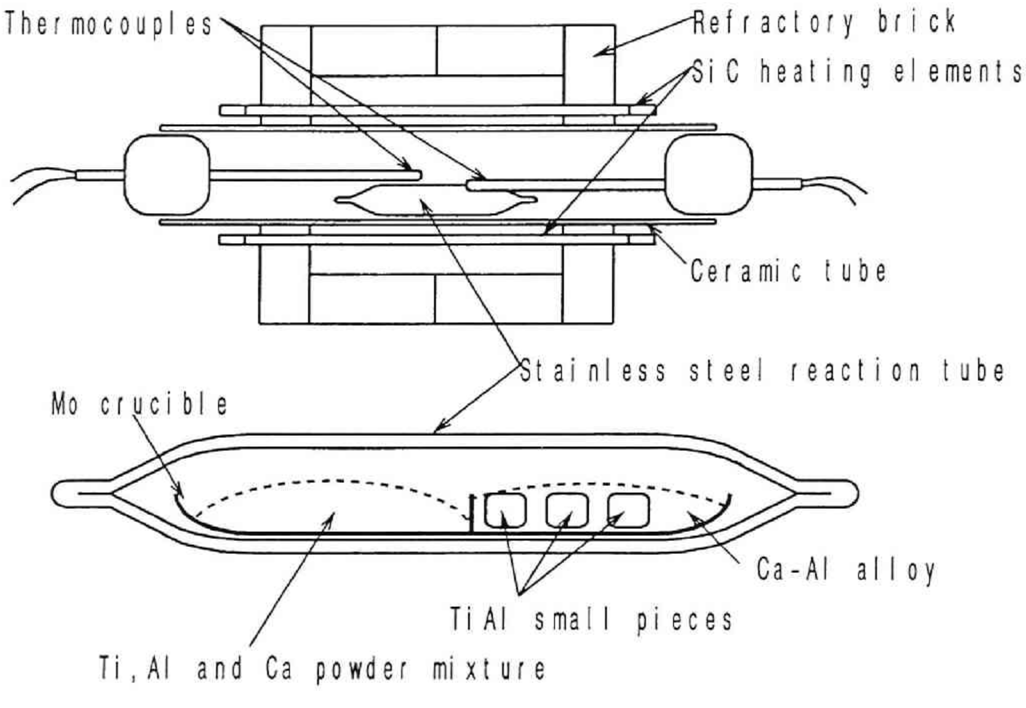


Figure 1.5: Schematic illustration of the experimental apparatus.

1.3 Results

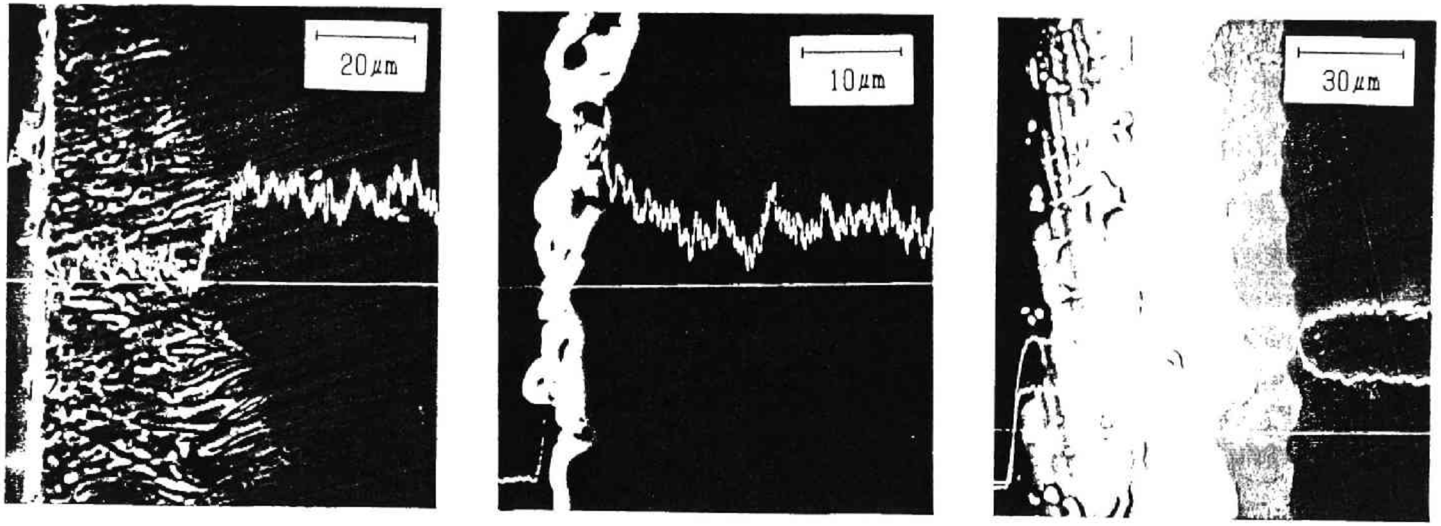
1.3.1 Reaction between TiAl and Ca–Al alloys at 1273K

Figure 1.6 shows some typical compositional and morphological changes of TiAl small pieces reacted with Ca–Al alloys of various compositions at 1273K for 86.4ks. The surfaces running vertically on the left hand side of the photographs mark the interfaces between TiAl sample and Ca–Al alloy which was removed by leaching. In the case of reaction between TiAl and pure calcium, as shown in Figure 1.6 (a), aluminum near the surface of the sample reacted with liquid calcium to form Ca–Al alloy. As a result, aluminum depletion occurred and porous Ti_3Al phases were formed in the vicinity of the surface. In the case of reaction with Ca–50mol%Al, as shown in Fig.2 (b), no intermetallic compound other than TiAl is observed. Thus it is demonstrated that Ca–50mol%Al can equilibrate with TiAl at 1273K. It is worth noting that even though TiAl was in equilibrium with Ca–50mol%Al alloy, the originally planar surface of the TiAl sample became gouged, as can be seen in Figure 1.6 (b). In the case of reaction between TiAl and Ca–67mol%Al, aluminum from the Ca–Al alloy diffused into TiAl to form aluminum–rich alloys such as $TiAl_2$ and $TiAl_3$, as shown in Figure 1.6(c).

Phase equilibria between TiAl and Ca–Al alloys were thus determined in this way. In addition to the diffusion couple experiment, isothermal annealing of metal powder mixtures of various initial composition was performed to verify the results of phase equilibria.

1.3.2 Phase diagram of the Ti–Al–Ca system at 1273K

Results of this type of experiment for the Ti–Al–Ca system at 1273K are compiled in Figure 1.7. This phase diagram was determined by more than a hundred isothermal annealing and diffusion couple experiments. Most of the phases present were identified by XRD and XMA. The experimental phase equilibria in Figure 1.7 were drawn supposing that the compositions of the liquidus equilibrating with $CaAl_2$ are 58.0 and 76.5mol%Al as shown in the binary phase diagram[2]. It was confirmed that titanium aluminides and Ca–Al alloys are mutually insoluble, as it was not



(a) (b) (c)

Figure 1.6: Scanning electron micrographs of sectioned TiAl small pieces reacted with various Ca–Al alloys at 1273K for 86.4ks. Composition of Ca–Al alloys were: (a) pure calcium, (b) Ca–50mol%Al and (c) Ca–67mol%Al.

detected by XMA. Both the titanium content in Ca–Al alloys and the calcium in Ti–Al alloys were found to be less than 0.3mol% by chemical analysis.

After the identification of the solid phases by XRD measurement, the Ca–Al alloys were extracted from the annealed specimens by leaching. The analyzed concentrations of the liquid Ca–Al were, however, scattered within 10mol%Al from the expected composition calculated from initial composition because of the creeping from the crucible and of the reaction with the crucible and atmospheric moisture.

The phase diagram in Figure 1.7 illustrates that Ca–Al alloy of aluminum concentration between 20.2 and 46.5mol%, equilibrates with TiAl at 1273K. It should be noted that there is some uncertainty in the aluminum concentrations of the Ca–Al alloys which equilibrate with α–titanium and β–titanium, namely Ca–1.11mol%Al and Ca–3.22mol%Al alloys in Figure 1.7.

1.4 Discussion

1.4.1 Activities of components in Ti–Al alloys

From the phase diagram of the Ti–Al–Ca system at 1273K evaluated in Figure 1.7, the activities of aluminum in the two phase region of Ti–Al system can be deduced from thermodynamic data of the Ca–Al system.

Previous study by Suzuki *et al.*[5] reported the calculated phase diagram of the Ti–Al–Ca system based on the thermodynamic evaluations from the literatures, where the activities in Ca–Al liquid alloy were extrapolated to 1273K using high temperature data at 1623K[6] by the regular solution approximation. Estimation of aluminum activity by Suzuki *et al.* seems to include large uncertainty due to the wide extrapolation of temperature.

Jacob *et al.* have recently reported the activities of calcium and aluminum in the liquid Ca–Al alloys at 1373K[7]. The activities of the Ca–Al system at 1273K, therefore, can be evaluated in fairly good accuracy using the reported thermodynamic values[7].

By treatment of the aluminum activities of Ca–Al alloys at 1373K using the regular solution model, activities of aluminum in the Ca–Al system at 1273K were calculated as shown in Figure 1.8. In this calculation it was assumed that solid

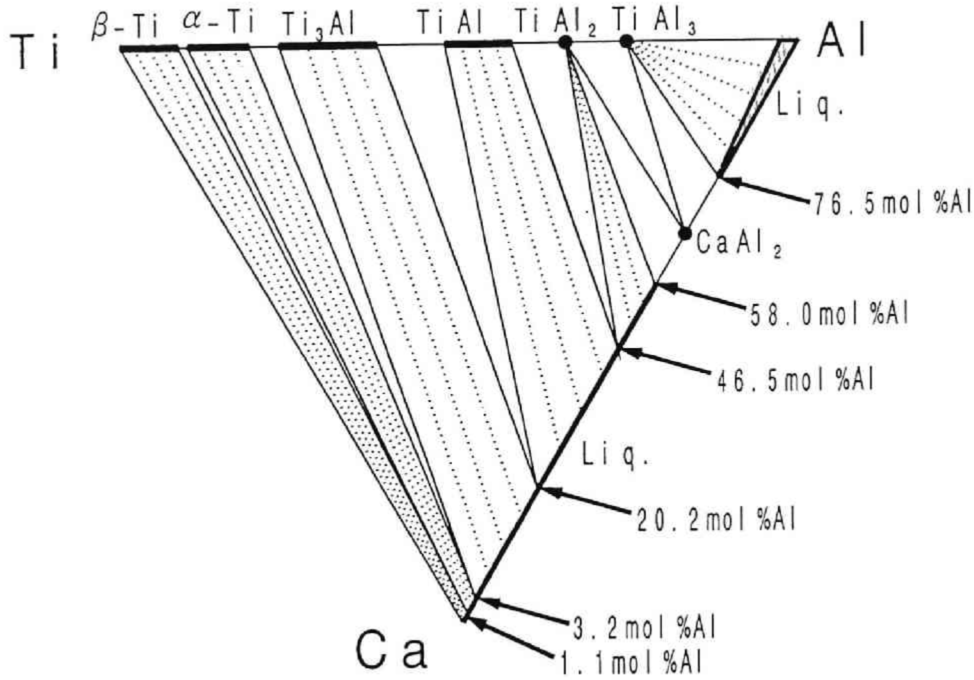


Figure 1.7: Phase diagram of the Ti–Al–Ca system at 1273K.

$CaAl_2$ exists in the Ca–Al system at 1273K in the composition range between 58.0 and 76.5 mol%Al, as can be read from Figure 1.3. Activities of Ca–Al liquid alloy at 1623K obtained by Schürmann[6] were not used for this calculation because these data are obtained at fairly high temperatures compared to the temperature studied in this work.

Combining the obtained phase diagram of the Ti–Al–Ca system at 1273K shown in Figure 1.7 and the calculated activities of Ca–Al system at 1273K, some aluminum activities in the two phase region in the Ti–Al system were estimated as shown in Figures 1.9 and 1.10. Aluminum concentrations corresponding to phase boundaries along the Ti–Al binary system at 1273K were read directly from the phase diagram proposed in Figure 1.2[1].

Titanium activities of the Ti–Al system at 1273K were also calculated by the Gibbs–Duhem integration on the assumption that the activity of aluminum in the titanium solid solution obeys Henry's law, and that activities of aluminum in titanium aluminides change linearly with the aluminum concentration. These results are shown both in Figures 1.9 and 1.10.

The standard free energies of formation of the Ti_3Al, TiAl and $TiAl_2$ at 1273K were calculated and are listed in Table 1.1 for reference. The titanium and aluminum activities between $TiAl_2$ and TiAl3, which is depicted as dashed line in Figures 1.9 and 1.10, were calculated by using the calculated standard free energy of formation of $TiAl_2$ in this study and the reported standard free energy of formation of $TiAl_3$ [10]. These values calculated in this study may be subject to rather large uncertainty for reason of analytical error of aluminum concentrations. Therefore, meaningful discussion of these values with the reported data [8][10] is reserved for the future.

1.4.2 Phase diagram of the Ca–Al–O system at 1273K

The extrapolated activities in the Ca–Al system can be used for the calculation of the phase equilibria and the conjugation lines in the Al–Ca–O system. The results are shown in Figure 1.11, where the other thermodynamic values used in this calculation are the same as the estimation by Suzuki *et al.*[5]. $Ca_{12}Al_{14}O_{33}$ was thought to be unstable[9] and omitted in the paper reported by Suzuki *et al.*[5] but it is taken into account in Figure 1.11 on the base of the thermodynamic data[9][11].

Jacob *et al.*[7] showed that CaO crucible was not suitable to hold the Al–rich Ca–Al liquid alloys, and they suggested that the complex oxides such as $CaAl_2O_4$

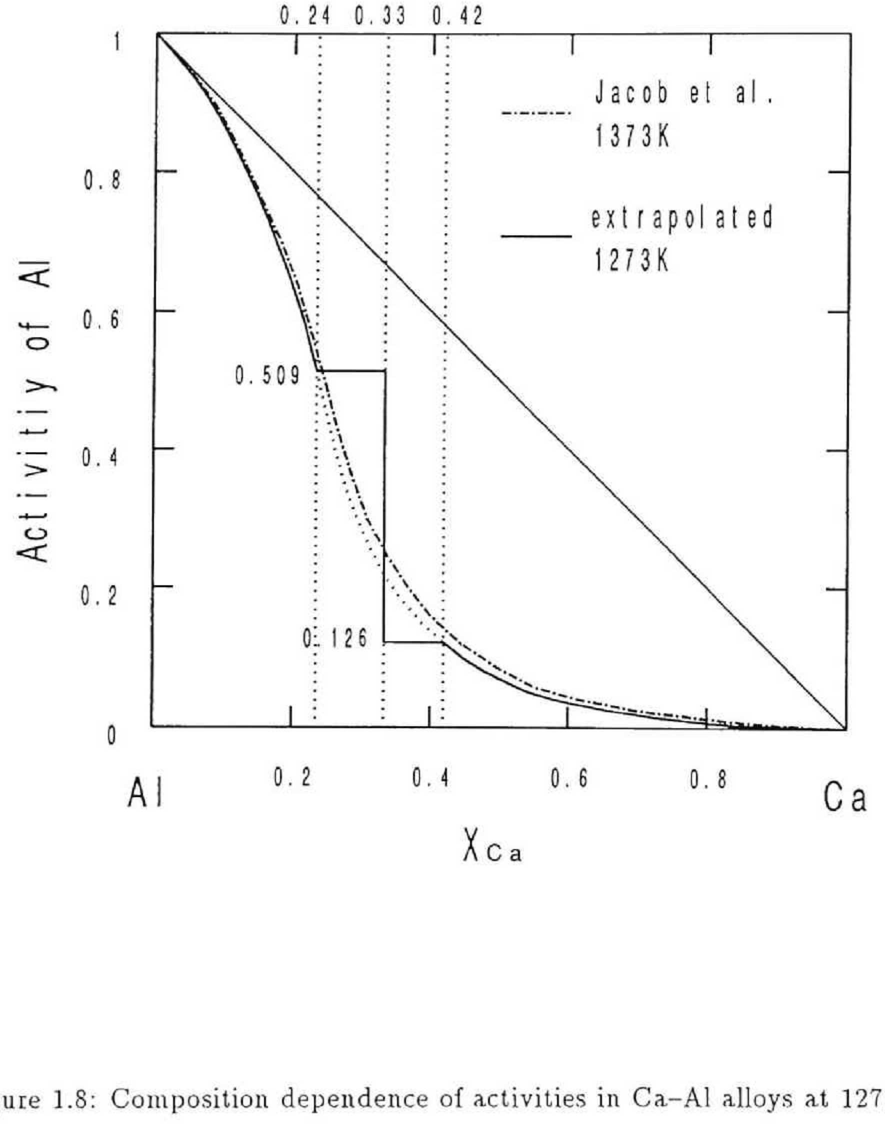


Figure 1.8: Composition dependence of activities in Ca–Al alloys at 1273K.

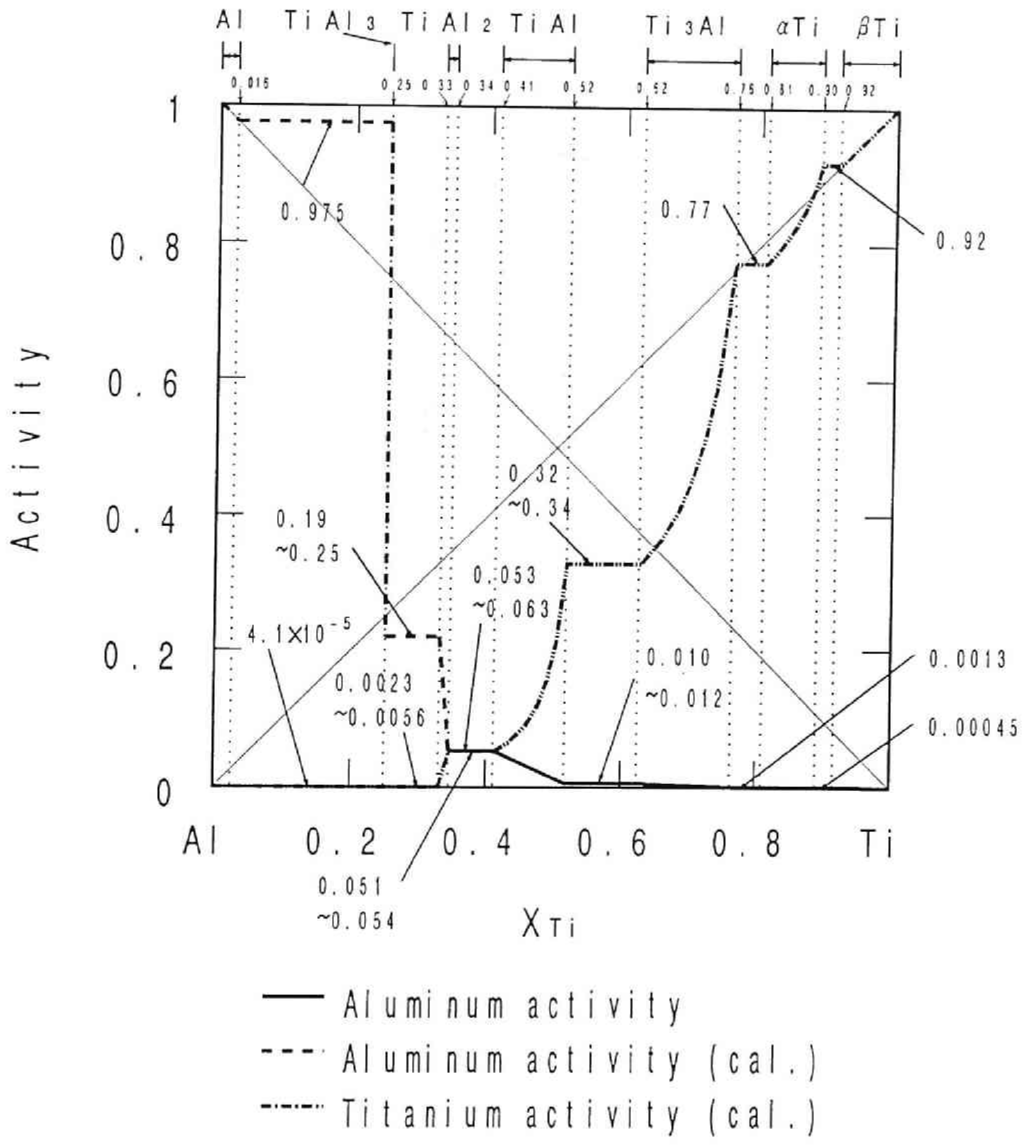


Figure 1.9: Composition dependence of activities in Ti–Al alloys at 1273K in liner scale.

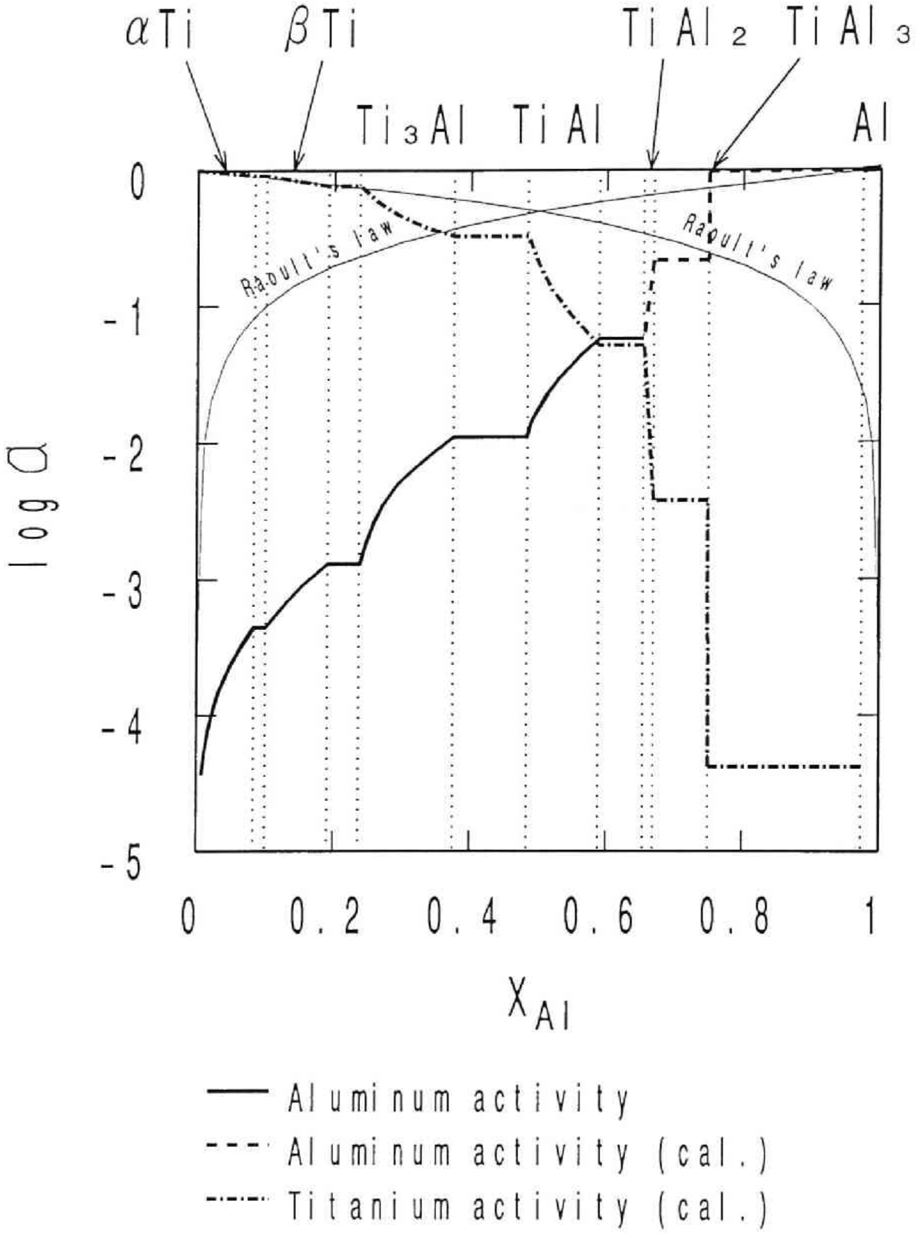


Figure 1.10: Composition dependence of activities in Ti–Al alloys at 1273K in logarithmic scale.

Table 1.1: Standard free energy of formation of titanium aluminide at 1273K.

	ΔG° / kJ mol^{-1}	
	This study	Kubaschewski[10]
Ti_3Al	−81	
TiAl	−61	
$TiAl_2$	−91	
$TiAl_3$		−108

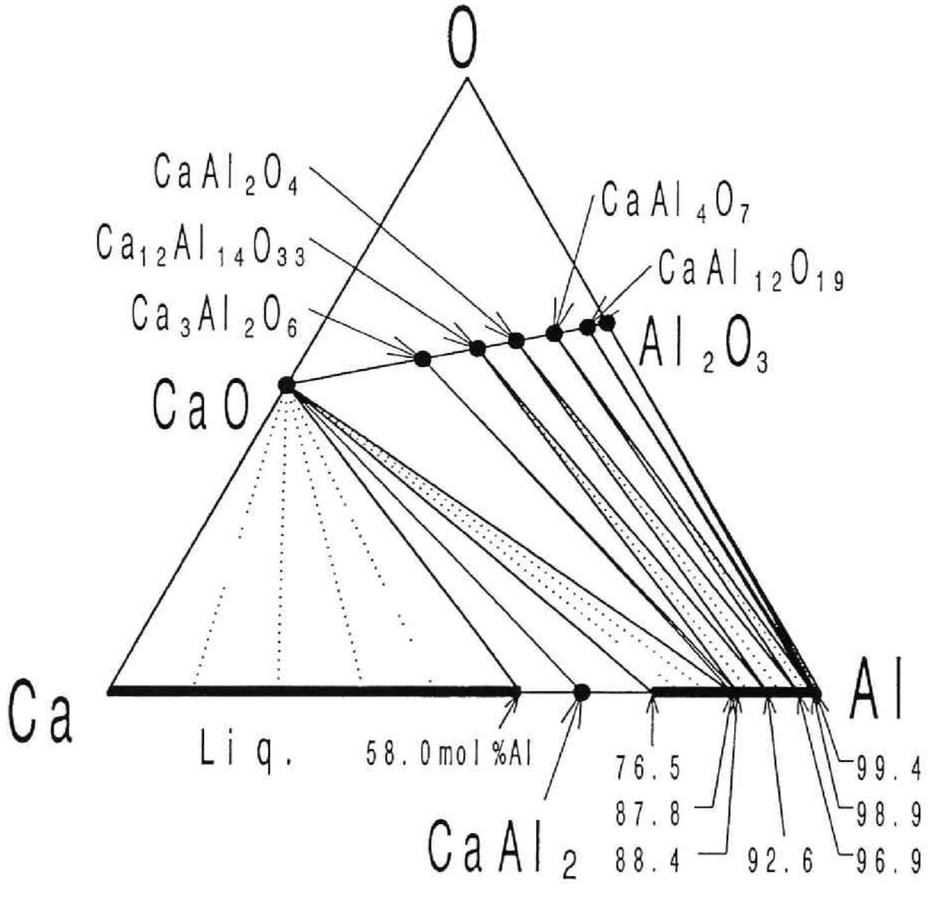


Figure 1.11: Phase diagram of the Ca–Al–O system at 1273K. The phase equilibria were estimated by the oxygen partial pressures and the activities using previous reports[5][6][7][9].

and $Ca_3Al_2O_6$ could be equilibrated with the Al–rich liquid. Their results strongly support the reliability of the calculation in Figure 1.11.

Figure 1.11 suggest an important indication that most of the Ca–Al alloys which equilibrate with titanium aluminides do not equilibrate with complex oxides between CaO and Al_2O_3. That is, reaction product of calciothermic reduction and deoxidation of titanium aluminides by Ca–Al alloys is in most cases CaO which can be easily removed by leaching. Ca–Al alloys with higher aluminum content than 87.8mol%, which equilibrate with $TiAl_3$, are not suitable for reductant or deoxidant because these alloys equilibrate with complex oxide (e.g. $Ca_3Al_2O_6$) which is difficult to remove by leaching. In the case of production of $TiAl_3$ by Ca–Al alloys, therefore, Ca–Al alloys containing between 67 and 88mol%Al is preferable as a residual reductant or deoxidant.

1.5 Conclusions

An investigation of phase equilibria of the Ti–Al–Ca system at 1273K was conducted to determine the compositions of Ca–Al alloys used as deoxidant suitable for the calciothermic deoxidation of titanium aluminides.

Results of the isothermal annealing and diffusion couple experiments in the Ti–Al–Ca system at 1273K showed that Ti_3Al, TiAl and $TiAl_2$ equilibrate with Ca–Al alloys between 3.2 and 20.2mol%Al, 20.2 and 46.5mol%Al, and 46.5 and 66.7mol%Al, respectively. $TiAl_3$ is in equilibrium with solid $CaAl_2$ or more aluminum richer Al–Ca liquid alloys at 1273K.

Based on these experimental phase equilibria and on the thermodynamic data in Al–Ca system, aluminum activities in the two phase region in the Ti–Al system at 1273K were estimated. Using these values, titanium activities of the Ti–Al system at 1273K were calculated by the Gibbs–Duhem integration, and standard free energies of formation of titanium aluminides at 1273K were also calculated.

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Chapter 2

Deoxidation of Titanium Aluminide by Ca–Al Alloy under Controlled Aluminum Activity

2.1 Introduction

In recent years, there has been considerable interest in developing titanium aluminide (TiAl) as a structural material, and mechanical properties of TiAl have been intensively investigated. In particular, plasticity of TiAl has proven to be influenced by impurities such as oxygen[1].

For laboratory use, the grade of TiAl is between 99.9% and 99.999% pure (excluding gaseous elements), where the main impurity is oxygen, at a level of at least several hundred mass ppm oxygen. This oxygen mainly originates from impurities in the titanium starting material which is produced by the Kroll process. Even though low oxygen-containing titanium has been successfully produced using other less-widely used methods, such as electrolytic refining or iodide refining methods, oxygen contamination of TiAl is inevitable during subsequent processing. Oxygen removal directly from TiAl to a level below 100 mass ppm is deemed to be very difficult, because TiAl has a strong affinity for oxygen. For this reason, titanium and aluminum are usually alloyed to make titanium aluminide in an oxygen-free atmosphere, taking great care to avoid oxygen pick up.

From a thermodynamic view point, external gettering used in solid state refining is one of the most promising methods for direct deoxidation of titanium and its alloys. In the previous part, the author has developed several effective methods for the deoxidation of titanium by using calcium–saturated halide flux. The titanium produced contains below 50 mass ppm oxygen. In the present study, one of these methods has been applied to the deoxidation of TiAl on the basis of an investigation of the phase equilibria of the Ti–Al–Ca system at 1273K conducted in the previous chapter.

2.2 Principles

Deoxidation of TiAl by reaction with a chemically–active element, namely calcium, through surface contact has been examined in the temperature range 1273 to 1473K, to obtain low oxygen–containing TiAl. Calcium is thought to be the most effective deoxidation agent not only because it has an extremely strong affinity for oxygen but because it has relatively high vapor pressure around 1273K (P_{Ca}=1.9kPa)[2]. Furthermore, the deoxidant calcium and the reaction product CaO can be easily removed by acid treatment.

Since the principle of deoxidation of titanium using calcium has been reported in detail in chapter 2 of part II, only a brief outline will be given here. Oxygen dissolved in TiAl can be removed by calcium according to the following reaction:

$$\text{O (in TiAl)} + \text{Ca (in Ca–Al)} = \text{CaO (in flux)} \qquad (2.1)$$

Co–existence of calcium and the reaction product, CaO, fixes the equilibrium oxygen partial pressure, and hence, the amount of residual oxygen in TiAl is thermodynamically fixed. As there is no available information on activity of oxygen in TiAl, the deoxidation limit of TiAl cannot be estimated with any great accuracy; however, the activity coefficient of oxygen in TiAl is believed to be larger than that in pure β–titanium considering the affinities of oxygen for titanium and aluminum and the solubilities of oxygen in titanium and aluminum. For this reason, the deoxidation limit of TiAl can be expected to be lower than that of titanium under the same oxygen partial pressure. From the fact that titanium could be deoxidized to a level below 100 ppm as shown in chapter 3 of part II, the deoxidation of TiAl to this level may be possible by decreasing the activity of CaO.

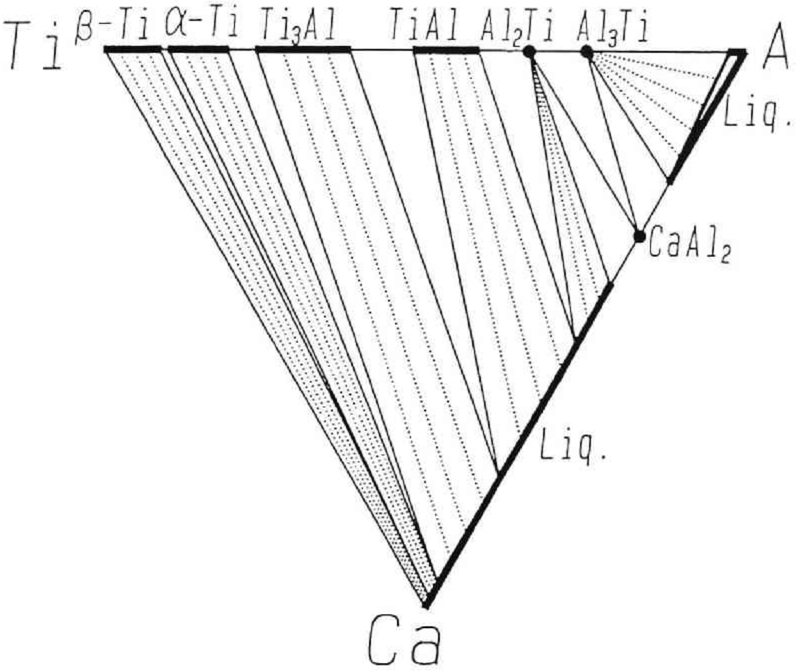

Figure 2.1: Phase diagram of the Ti–Al–Ca system (in mol% scale) at 1273K.

Similar to the previous studies carried out in part II, $CaCl_2$ was used as a flux to dissolve the deoxidation agent calcium and, in addition, to facilitate the deoxidation reaction by diluting the reaction product CaO, i.e., by decreasing the activity of the by-product CaO.

Results of phase relation between TiAl and Ca–Al alloys, which were established in the previous chapter, indicate that Ca–Al alloy of aluminum concentration between 20 and 50mol%, equilibrates with TiAl at 1273K, as shown in Figure 2.1. For oxygen extraction to a very low level, higher calcium concentration is preferred; however, high aluminum content alloys (about 50mol%Al) were mainly employed as deoxidants in this study, to compensate for subsequent aluminum depletion of the alloy during reaction with metallic assemblies of the reaction tube.

2.3 Experimental

2.3.1 Deoxidation of TiAl by Ca–Al alloys

Figure 2.2 shows the arrangement of the reaction tube used in this study for the deoxidation of TiAl. Specifications and chemical analysis of the feed materials are detailed in Table 2.1. These TiAl samples, as well as Ca–Al alloys, were put in a titanium crucible as shown schematically in Figure 2.3 (a). In some experiments, TiAl powder which had been thoroughly mixed with CaO powder, was contained in a titanium cup (Figure 2.3 (b)). In other experiments, TiAl in the form of powder and small pieces (about 20–40g) was placed on a titanium dish within a titanium cup, which was filled with about 20g of $CaCl_2$ powder (Figure 2.3 (c)). The anhydrous $CaCl_2$ and CaO used were reagent grade (99.9%) powders dried for more than 200ks at 800K and for more than 100ks at 1300K, respectively, before use. For the purpose of monitoring the oxygen partial pressure, small pieces of pure titanium (about 0.3g each) were set together with the TiAl samples in some experiments. Cups containing sample and flux were sealed in a stainless steel tube in addition to a mixture of calcium and aluminum granules, as shown in Figure 2.2. The total amount of calcium and aluminum was about 15g, and the initial composition of the Ca–Al alloy was varied from Ca–40mol%Al to Ca–60mol%Al, which was the composition range shown to be favorable for deoxidation of TiAl by the phase equilibrium experiments carried out in chapter 1. To avoid contamination by impurities present in calcium, especially nitrogen, calcium–aluminum alloy was isolated from the samples, and supplied to the samples in vapor form.

The assembled sealed tube was heated in an electric furnace to a temperature between 1273 and 1473K. The holding time was between 86.4ks and 260ks, after which the reaction tube was removed from the furnace and quenched in water.

After the deoxidation, the Ca–Al alloy, CaO and/or $CaCl_2$ in the titanium cup was removed by leaching with (1+1) acetic acid, and the remaining TiAl sample was carefully cleaned in warm aqueous HCl solution followed by water, alcohol and acetone rinses, and then allowed to dry under vacuum.

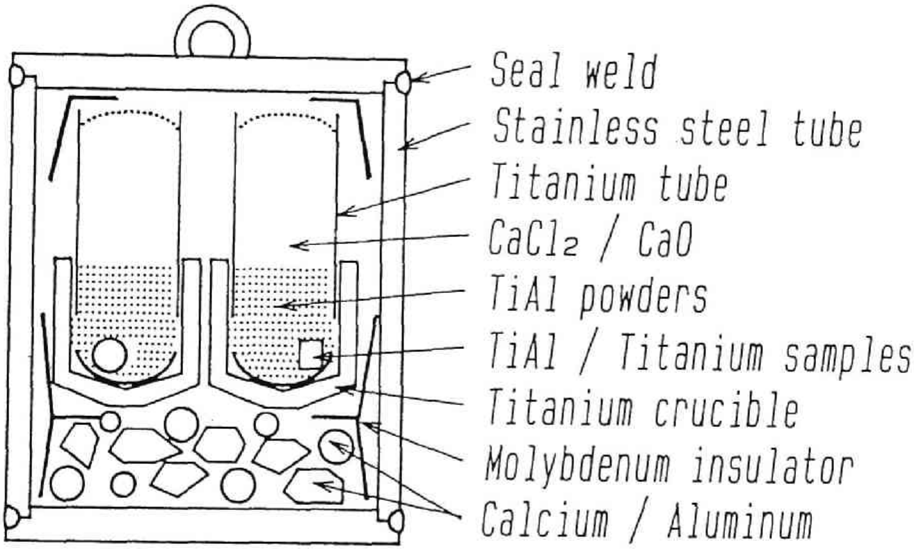

Figure 2.2: Schematic illustration of reaction tube used for deoxidation of TiAl.

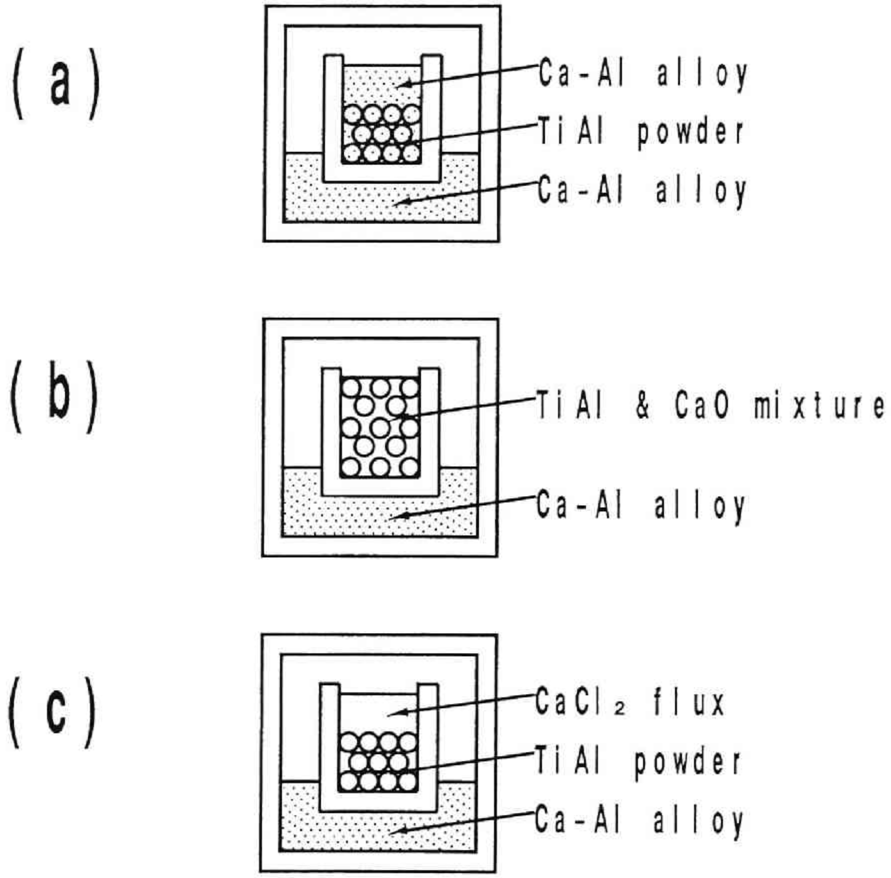

Figure 2.3: Variation of deoxidation method of TiAl by Ca–Al alloys.

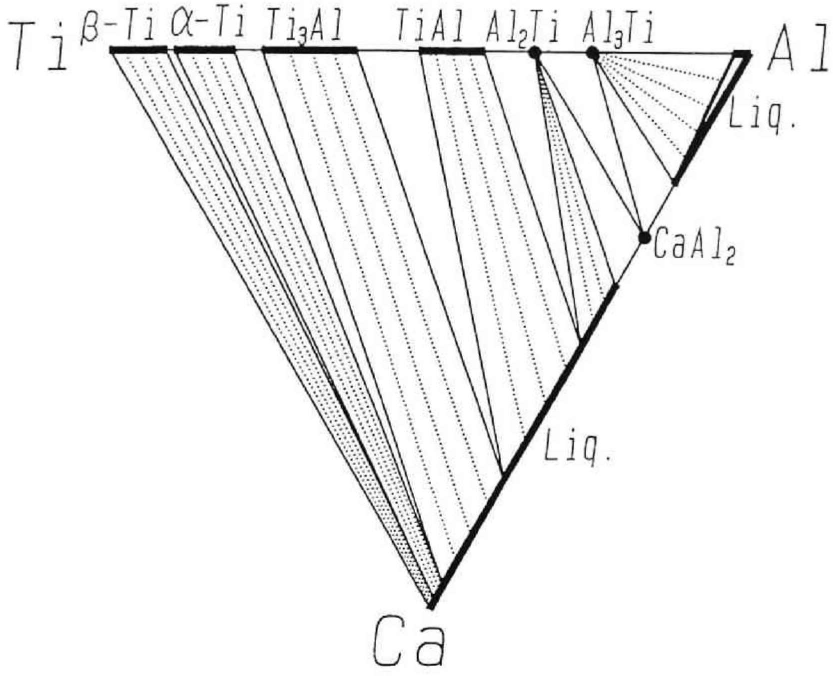

Figure 2.1: Phase diagram of the Ti–Al–Ca system (in mol% scale) at 1273K.

Similar to the previous studies carried out in part II, $CaCl_2$ was used as a flux to dissolve the deoxidation agent calcium and, in addition, to facilitate the deoxidation reaction by diluting the reaction product CaO, i.e., by decreasing the activity of the by-product CaO.

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After the deoxidation, the Ca–Al alloy, CaO and/or $CaCl_2$ in the titanium cup was removed by leaching with (1+1) acetic acid, and the remaining TiAl sample was carefully cleaned in warm aqueous HCl solution followed by water, alcohol and acetone rinses, and then allowed to dry under vacuum.

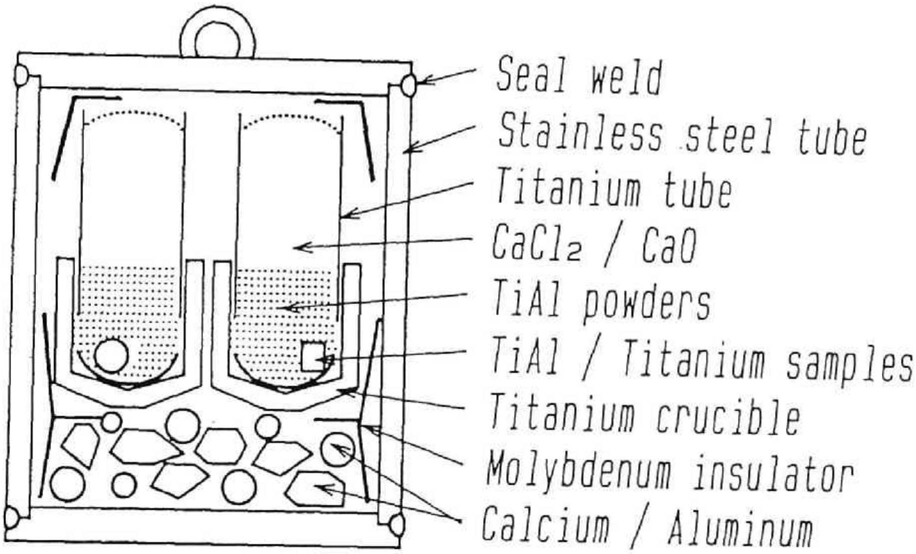

Figure 2.2: Schematic illustration of reaction tube used for deoxidation of TiAl.

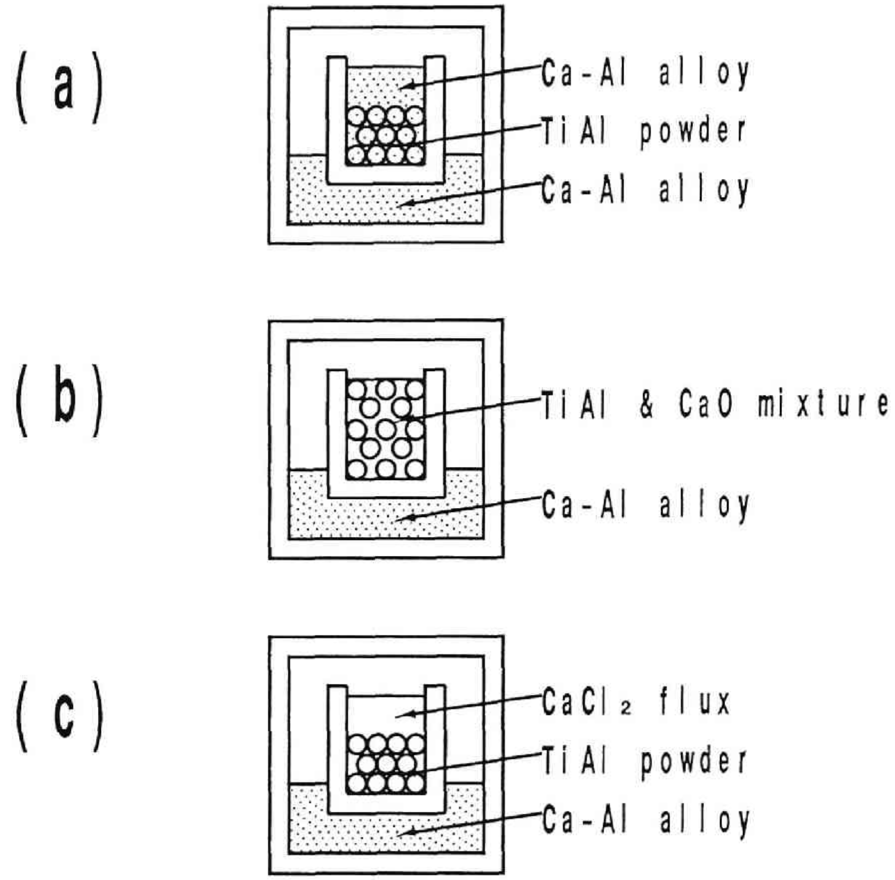

Figure 2.3: Variation of deoxidation method of TiAl by Ca–Al alloys.

Table 2.1: Starting material used in this study.

Samples	Purity+ (%)	Oxygen (mass ppm)	Nitrogen (mass ppm)	Titanium (mass%)[mol%]	notes
TiAl powder*	99.9	510	70	64.0 [50.1]	42~60 mesh
TiAl powder*	99.9	1100	30	65.0 [51.2]	-60 mesh
TiAl powder*	99.9	4200	50	65.6 [51.8]	-60 mesh
TiAl small pieces	99.9	1000	150	63.5 [49.5]	~0.5g each
Ti small pieces	99.99	200	30	100 [100]	~0.3g each

* : Produced by the plasma roatated electrode process.

† : Excluding gaseous elements.

2.3.2 Analysis

Oxygen and nitrogen analyses of samples were made using an inert gas fusion infrared absorption method (LECO TC–336 analyzer). Especially in the case of small pieces of titanium, the samples were mechanically polished, and then chemically polished with a 1:4:10 mixture of $HF:HNO_3:H_2O$ to remove the aluminized surface. 0.1g of TiAl sample, mostly in powder form, was sealed in a tin capsule and wrapped in 1g of platinum foil. The sample was then dropped into a graphite crucible which was held at a temperature above 2800K, for the purpose of oxygen and nitrogen extraction. The analyzer was calibrated by using standard iron samples containing 77 and 82 mass ppm oxygen and nitrogen, respectively, and the measured values were cross checked with different standard titanium samples (e.g. 440 mass ppmO and 20 mass ppmN). The average blank values of oxygen and nitrogen (arising mainly from the platinum and tin bath) were $4.5\pm2.0\mu g$ and $0.3\pm0.1\mu g$, respectively. In some analyses, 1g of nickel was used as the bath for oxygen extraction. The average blank values of oxygen and nitrogen of the nickel bath were $12\pm4\mu g$ and $1.0\pm0.3\mu g$, respectively. To ascertain the accuracy of the analyzed values of oxygen, oxygen analysis of some samples was performed independently by a company.

Titanium and calcium concentrations of the sample were determined by an electrothermal atomizer (flameless) atomic absorption spectrometric method.

Identification of the existing phases in the sample was carried out by powder X-ray diffractometry(XRD) using a Philips PW1700 system. X-ray microprobe analysis (XMA, Hitachi X-650) was done to obtain the compositional profiles.

2.4 Results and Discussion

2.4.1 Deoxidation of TiAl in liquid Ca–Al alloys

The analyzed oxygen concentrations of the small pieces of TiAl, used also in the diffusion couple experiments in chapter 1, which reacted with Ca–50mol%Al at 1273K, were in most cases about 1000 mass ppm, and did not vary much from the initial value. In some cases, there was an increase but with large scatter. The reaction time and the composition of the Ca–Al alloys did not appear to influence the final oxygen concentration of the TiAl small pieces. This is probably due to a low rate of oxygen diffusion in TiAl, and the increase in oxygen level may be due to oxygen pick up from impurities trapped on the rough surface as indicated in Figure 1.6 (b) in chapter I in this part.

When the reaction temperature was raised to 1373K, the TiAl small pieces (initial concentration of 1000 mass ppm oxygen) were, in some cases, deoxidized to a several hundred mass ppmO using Ca–50mol%Al and a reaction time of 86ks. Based on these results, the reaction temperature was raised to 1373K or 1473K with the purpose of shortening the reaction period. Moreover, TiAl samples in powder form (see Table 2.1) were mainly used to diminish the problem of slow oxygen diffusion.

In the deoxidation experiments at 1373K and even more so at 1473K, aluminum depletion by reaction with the stainless steel reaction tube became pronounced. The aluminum concentration in Ca–Al alloys decreased by 5 to 20 mol% at 1373K, and this decrease was more significant at 1473K. The initial composition of Ca–Al alloy adopted in subsequent deoxidation experiments was, therefore, Ca–60at%Al to compensate for aluminum depletion from the alloys.

A scanning electron micrograph of the TiAl powder used as starting material in this study is shown in Figure 2.4 (a). Morphology typical of TiAl powder

(Exp.No.33–liq) which had been reacted in liquid Ca–Al alloy at 1373K for 86.4ks and then acid leached to remove Ca–Al alloys, is displayed in Figure 2.4 (b). The photographs in Figure 2.4 demonstrate a change in the surface of the TiAl spheres from planar to nodular, following reaction in liquid Ca–Al alloy. The concentration of aluminum in the TiAl powder remained unchanged, whereas the composition of the Ca–Al alloy co-existing with the powders of TiAl changed to Ca–53mol%Al as determined by XMA analysis. The average oxygen concentration of the TiAl powder which was initially 4200 mass ppm (refer to Figure 2.4) decreased to 870 mass ppm with a scatter of about 90 ppmO about the average analytical value. Measured oxygen concentrations, are listed in Table 2.2 (Exp.No.33–liq). Nitrogen concentrations of the deoxidized sample increased by 50 to 200 mass ppm, randomly. The large scatter in oxygen and nitrogen concentrations is probably due to impurities trapped on the rough particle surface.

The method described above proved to be effective in deoxidizing TiAl to a low level, however the resulting nodular surface led to trapped impurities.

2.4.2 Deoxidation of TiAl in CaO powder by Ca–Al vapor

After deoxidation by Ca–Al vapor of TiAl powders mixed with CaO, a soft yellow cake was obtained. A scanning electron micrograph of the cross-sectioned cake which had been reacted at 1373K for 86.4ks, is shown in Figure 2.5 (a). Characteristic X-ray images corresponding to Figure 2.5 (a) show that the cake was a mixture of TiAl powder, CaO and Ca–Al alloy. The micrographs illustrate that TiAl and Ca–Al alloys are mutually insoluble. The composition of TiAl powder did not change after reaction, and the composition of Ca–Al liquid alloy remaining in the bottom of the reaction tube was about Ca–53mol%Al. The CaO and Ca–Al alloy in the cake could be easily removed from the TiAl powders by leaching in acid. Fine TiAl particles were obtained as shown in Figure 2.5 (f).

In the case where TiAl powders were isolated from liquid Ca–Al alloy by using CaO powder, and deoxidation was effected by Ca–Al vapor, particle surface irregularity was considerably less than that of powders submerged in liquid Ca–Al alloy. The oxygen concentration of the isolated powders decreased from 4200 ppm to about 670 ppm for a reaction period of 86.4ks, and the amount of scatter in oxygen concentration among the analyzed samples was small, as shown by Exp.No.33–M in Table 2.2. Furthermore, analytical values from various sampling points on the cake showed

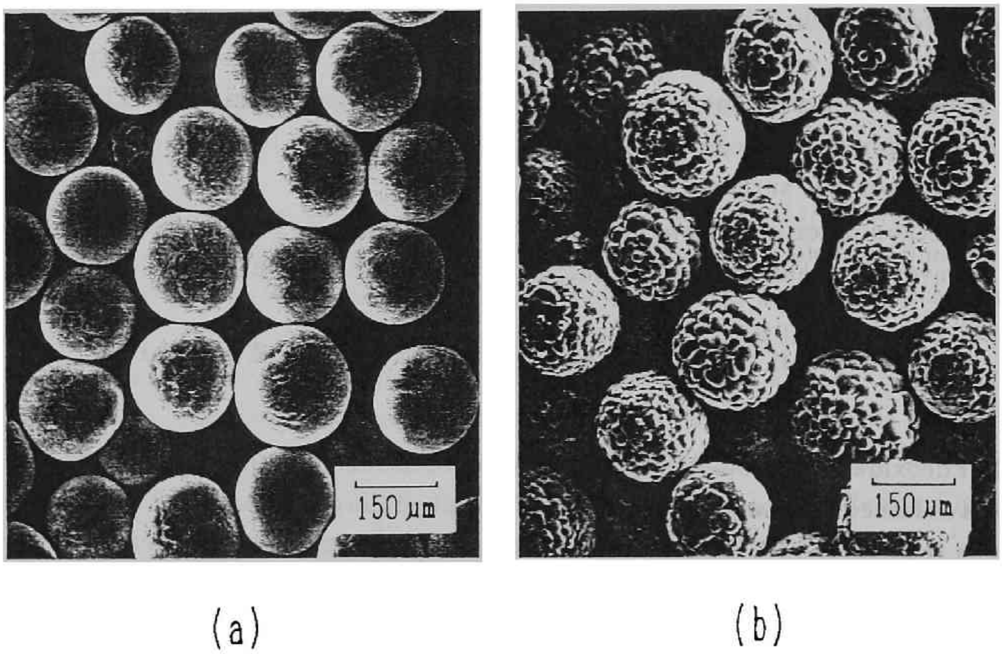

Figure 2.4: Scanning electron micrographs of TiAl powders produced by the plasma rotating electrode process: (a) starting material, and (b): after deoxidation in liquid Ca–Al alloy at 1373K for 86.4ks. Oxygen concentrations of TiAl powders before and after deoxidation were 4200 and 870 mass ppm, respectively.

Table 2.2: Analytical results of TiAl powders deoxidized by Ca–Al vapor at 1373K for 86.4ks using various fluxes.

Exp. No.	Flux	Oxygen conc. (mass ppm)		Titanium conc. (mass%)		Calcium conc. (mass ppm)
		Initial	After exp.	After exp. AA[1]	EPMA	After exp. AA[1]
38-U	$CaCl_2$	510	66[2], 73[2], 33, 69, 70[3]	63.9	64.5	150
38-L	$CaCl_2$ (see Fig. 2.6)	510	76[2], 87[2], 34, 48, 80[3]	63.9	64.0	160
39	CaO[4]	510	91[2], 80, 130[3]	62.1	61.1	220
39-ac	CaO[4]	510	85[2], 44		63.3	
35-1	$CaCl_2$	1100	110, 160, 110[3], 190[3]	65.7 65.3	63.2	250 250
35-2	$CaCl_2$[5]	1100	190, 200, 200[3]	64.5	64.1	270
35-3	CaO	1100	430, 450, 600[3]	64.9	65.3, 66.6	870
40	$CaCl_2$	4200	210[2], 150, 180, 230[3]	62.9	63.3	460
33-M	CaO (see Fig. 2.5)	4200	630[6], 660, 660[6], 660, 670, 700[6], 710		64.3 63.7[6]	
33-liq	Ca-Al liq. (see Fig. 2.4(b))	4200	780, 820, 920, 960		61.4 61.5	

1 : Analyzed by electrothermal atomizer(flameless) atomic absorption spectrometric method.
2 : Analyzed by inert gas fusion infrared absorption method using Pt bath.
3 : Analyzed by company A using Ni bath.
4 : $CaCl_2$ was added to CaO to facilitate reaction, and reacted for 260ks.
5 : 1g of aluminum granules were added to $CaCl_2$ flux before deoxidation.
6 : Samples were rinsed with acid twice.

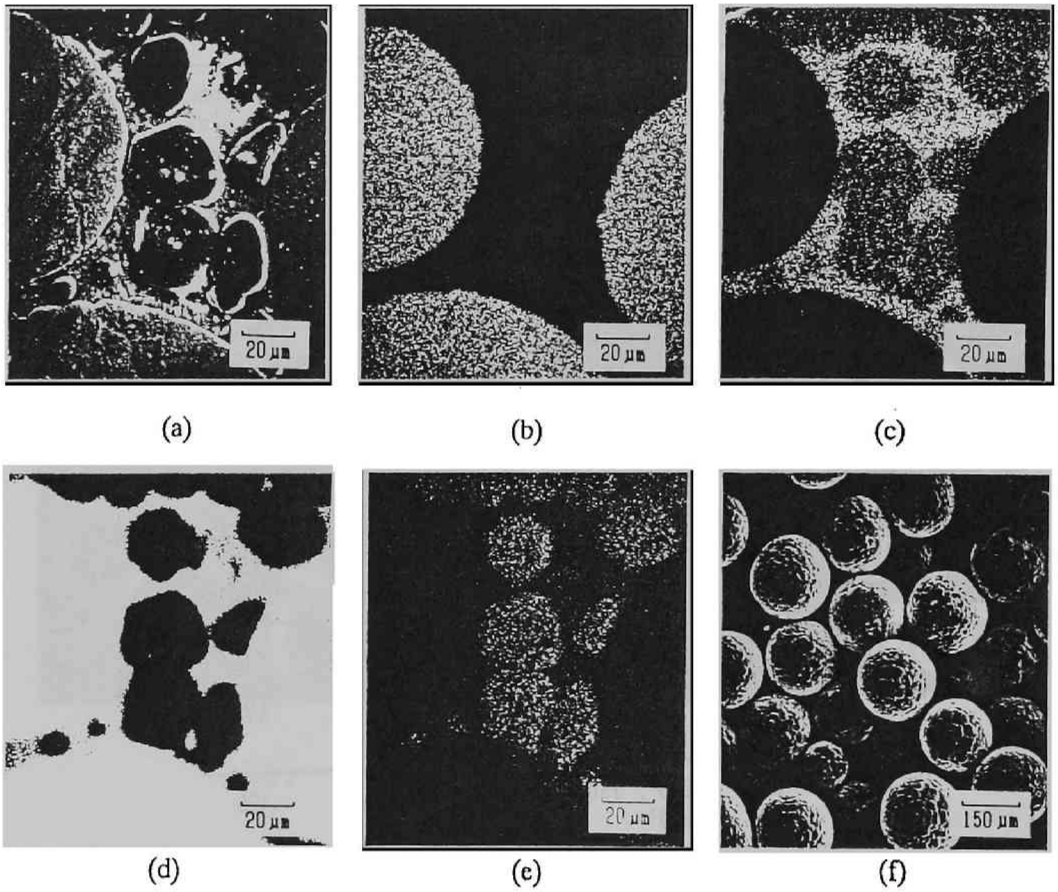

Figure 2.5: Scanning electron micrographs of TiAl powder – CaO mixture deoxidized by Ca–Al vapor, and corresponding elemental maps: (a) SEM image of mixture deoxidized at 1373K for 86.4ks. (b) titanium elemental map, (c) calcium, (d) aluminum, (e) oxygen, (f) SEM image of reacted TiAl following acid leaching to remove CaO and Ca–Al alloy. Average oxygen concentration decreased from 4200 mass ppmO to 670 mass ppmO, after reaction.

no significant difference, as demonstrated in the third column of results in Table 2.3. That is, powder sampled from the same cake can be considered homogeneous.

As shown by Exp.No.35–3 in Table 2.2, TiAl powders initially containing 1100 mass ppm oxygen were deoxidized to 400 to 600 ppmO, at 1373K for 86.4ks. The bulk titanium concentration of the powders, measured by flameless atomic absorption, did not change during deoxidation, while the surface concentration of titanium in the powders increased by 1 to 2 mass%, as determined by XMA. The difference between the bulk and surface analytical values cannot be fully discussed at this stage because factors such as aluminum depletion at the surface by acid leaching, and uncertainty in XMA results due to surface conditions, have yet to be quantified.

The results summarized in the second and third columns of Table 2.3 illustrate that a lower initial oxygen concentration of powder and a longer reaction time are to be desired in obtaining lower oxygen–containing TiAl powders. These results also indicate that the equilibrium oxygen concentration in TiAl was not reached under the present set of experimental conditions. This is probably due to a low rate of oxygen diffusion in TiAl.

Nitrogen concentration in the samples was independent of the experimental conditions, and increased from the initial value by about 50 mass ppm. Calcium concentration of the TiAl powders increased to several hundred mass ppm after deoxidation. A reaction time longer than 260ks was found to be undesirable not only because of surface aggravation of the TiAl powders, which leads to inclusion of impurities, but also because of aluminum depletion of the Ca–Al alloy. In the following section, therefore, $CaCl_2$ was used as a flux to facilitate the deoxidation reaction.

2.4.3 Deoxidation of TiAl in $CaCl_2$ by Ca–Al vapor

Following deoxidation, TiAl samples were found to be fused in $CaCl_2$ in the titanium cup. No metallic calcium from the Ca–Al alloy was detected on the surface of the fused salts, and no aluminum was present in the $CaCl_2$, as determined by XMA. This was the case even when 1g of small pieces of aluminum was added to the $CaCl_2$ flux before reaction(Exp.No.35–2). Fine TiAl particles were obtained after reaction for 86.4ks at 1373K. The fused salt was easily removed from the TiAl powders by acid. A reaction period greater than 100ks resulted in sintering of the TiAl particles, and removal of the flux by leaching was time consuming.

TiAl powders initially containing 510, 1100 and 4200 mass ppm oxygen were

Table 2.3: Results of deoxidation of TiAl powder using various methods*.

	Average oxygen concentration after deoxidation (mass ppm)			
Starting material	$CaCl_2$ flux Ca-Al vapor 86.4ks (1 day)	CaO flux Ca-Al vapor 260ks (3 days)	CaO flux Ca-Al vapor 86.4ks (1 day)	in liquid Ca-Al 86.4ks (1day)
TiAl powder 510 mass ppm	62 [38-U] 66 [38-L] 80 [40-ac] 110 [40] (see Fig. 2.6)	100 [39] 65 [39-ac]	160 [41]	
TiAl powder 1100 mass ppm	140 [35-1] 200 [35-2] 300 [36]	310 [37]	490 [35-3]	440 [36]
TiAl powder 4200 mass ppm	190 [40]		660 [33-U] 670 [33-M] 630 [33-L] (see Fig. 2.5)	870 [33] (see Fig. 2.4 (b))
Ti small pieces 200 mass ppm	890 [38] 360 [40]	3800 [39]	1500 [33] 1500 [35] 2500 [41]	1200 [33]

*: see Figure 2.3.

note: Values in square brackets denote the experimental number, and the suffixes denote the following experimental conditions;

-U, -M and -L : Sample taken from the upper, middle and lower part of the as-reacted cake, respectively.

-ac : Ca-Al alloys and/or fluxes were removed by using CH_3COOHaq. only.

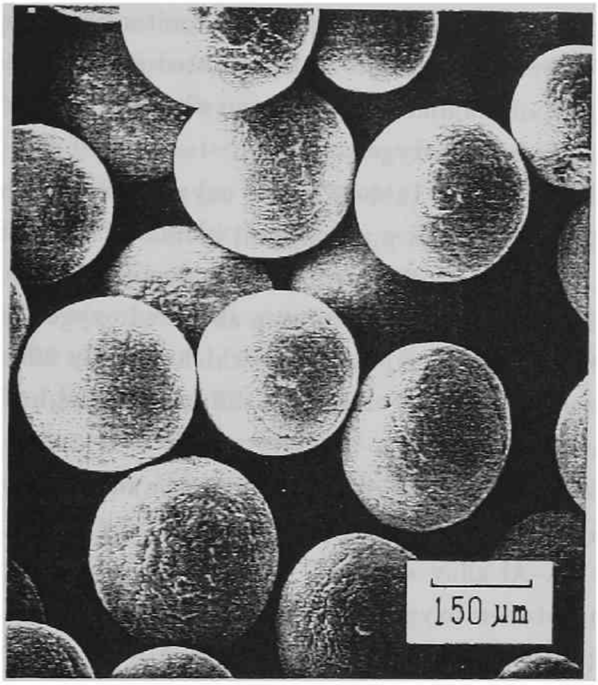

Figure 2.6: Scanning electron micrograph of TiAl powders deoxidized in $CaCl_2$ flux at 1373K for 86.4ks. TiAl powders, initially containing 510 mass ppmO, were deoxidized to about 70 ppm.

deoxidized to 62, 140 and 190 mass ppm as average value, respectively, by using $CaCl_2$ flux at 1373K, as shown by Exp.No.38–U, 35–1 and 40 in Table 2.3 (and also in Table 2.2 for detailed values). A scanning electron micrograph of deoxidized TiAl particles containing 66 mass ppmO as average value (Exp.No.38–L in Table 2.2 and 2.3) is presented in Figure 2.6. No significant change in morphology of the particle surface following deoxidation is observed. Titanium and nitrogen concentrations of the powder were unchanged, whereas calcium, initially present in trace amounts, increased to 160 mass ppm by the deoxidation treatment.

Among the many conditions investigated in this study, the method using $CaCl_2$ flux was the most effective in obtaining low–oxygen TiAl powders.

2.4.4 Oxygen potentials in the deoxidation of TiAl

In some experiments, small pieces of titanium were placed together with the TiAl powders, within the titanium cup, for the purpose of monitoring the oxygen partial pressure in the reaction tube. The surfaces of the reacted small pieces of titanium were aluminized to a depth of 0.3mm. This aluminized surface was removed both mechanically and chemically before oxygen analysis.

As shown in the bottom row of Table 2.3, the oxygen level in small pieces of titanium initially containing 200 mass ppm oxygen, increased in all cases after reaction. That is, oxygen potentials sufficient for TiAl deoxidation are ineffective in the deoxidation of titanium. The wide variation in analyzed oxygen concentrations may be attributed to changes in calcium activity which directly affect the oxygen potential in the system, or to a low rate of oxygen diffusion through the aluminized surface layer on the titanium sample.

Assuming that the diffusivity of oxygen in titanium and Ti–Al alloy is faster than that of aluminum in Ti–Al alloy, the oxygen potential of the Ti–O alloy should be equal to that of the Ca–Al alloy and CaO equilibrium. By using a previously determined relationship between oxygen concentration in Ti–O solid solution and oxygen potential in chapter 1 of part II, the oxygen potential in the present system was estimated to within an order of 10^{-32} Pa, in the presence of CaO at 1373K.

2.5 Conclusions

Removal of oxygen in titanium aluminide (TiAl) by reaction with chemically active calcium–aluminum alloy was carried out around 1373K with the purpose of obtaining extra–low–oxygen TiAl.

The deoxidation experiments were conducted on the basis of an investigation of phase equilibria of the Ti–Al–Ca system at 1273K which is mainly carried out in chapter 1. The compositions of Ca–Al alloys used as deoxidant, which equilibrate with TiAl, and the experimental conditions suitable for the deoxidation were examined.

In experiments in which Ti–Al samples were submerged in liquid Ca–Al alloys at 1373K, the surface of the samples severely deteriorated and became nodular. To prevent this surface deterioration, Ca–Al alloy deoxidant was, in most cases, supplied to the TiAl samples in vapor form. As oxygen diffusion in TiAl is slow, samples in powder form were mainly used in the deoxidation experiments to minimize the time required for reaction.

When TiAl powder was mixed with CaO, and the deoxidant was supplied in vapor form, powders initially containing 510, 1100 and 4200 ppmO were deoxidized to about 160, 490 and 670 ppmO, respectively, after deoxidation at 1373K for 86.4ks.

Among many conditions tested, utilization of TiAl powders mixed with $CaCl_2$ proved to be the most effective for deoxidation at 1373K. $CaCl_2$ was used as a flux to facilitate the deoxidation by decreasing the activity of the reaction product CaO. TiAl powders mixed with $CaCl_2$ and reacted with Ca–Al vapor at 1373K for 86.4ks, were deoxidized to levels of 62, 140 and 190 mass ppmO from initial concentrations of 510, 1100 and 4200 mass ppmO, respectively. No significant change in morphology of the particle after deoxidation was observed. The titanium and nitrogen concentrations of the powders remained unchanged, whereas calcium, initially present in trace amounts, increased to 160 mass ppm by the deoxidation treatment.

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Chapter 3

Preparation of TiAl and Ti_3Al Powders by Calciothermic Reduction of Oxides

3.1 Introduction

In the last ten years, there has been the extensive interest in titanium–aluminum intermetallic compounds, Ti_3Al, TiAl and $TiAl_3$, as structural materials. The consolidated parts made of the alloy powders by HIP– or CIP– vacuum sintering are very useful, therefore development of effective methods of producing these alloy powders is essential. A novel method of producing TiAl and Ti_3Al powders by calciothermic reduction of oxide mixtures was investigated in this chapter.

So far the direct compound reduction techniques, called the co–reduction and reduction–diffusion (RD) processes, have been successfully used for the preparation of permanent magnetic materials, such as Sm–Co[1]–[3] and Nd–Fe–B[4][5], and the superconducting Nb_3Sn powders[6]. Previously Suzuki *et al.* briefly reported that Ti–Al alloy powder can be obtained from the mixed oxides using by the co–reduction technique by Ca vapor[7]. The obtained powder was very fine, since calciothermic reduction of oxides produces alloy powder at low temperatures without melting. The chemical reactions to produce TiAl and Ti_3Al from oxides can be described by the equations:

$$2\ TiO_2 + Al_2O_3 + 7\ Ca = 2\ TiAl + CaO \tag{3.1}$$

$$6\ TiO_2 + Al_2O_3 + 15\ Ca = 2\ Ti_3Al + 15\ CaO \tag{3.2}$$

CaH_2 is also available for the reduction of TiO_2 and Al_2O_3 because of its strong affinity with oxygen. This has been used to produce Sm–Co and Nd–Fe–B magnets by the co–reduction or RD process[3][8]. These reactions are characterized by starting from easily available oxides, but there are some difficulties[7] depending on: (1) removal of oxygen to the level satisfying the commercial standards, (2) single phase preparation, and (3) stoichiometry control of the compounds. It should be noted that titanium and calcium are mutually insoluble[9], while calcium and aluminum may form a liquid alloy or $CaAl_2$ at the reduction temperature[10] as indicated in chapter 1.

The report on the calciothermic reduction of titanium and aluminum oxides by Suzuki *et al.* mainly dealt with the preparation of Ti– dilute Al alloys[7]. In this study, the results of experimental investigations directed towards the production of clean TiAl and Ti_3Al compounds by the co–reduction process using calcium hydride in addition to calcium are discussed.

3.2 Experimental

Two non–stoichiometric phases, Ti_3Al and TiAl, and a stoichiometric $TiAl_3$ are present in the Ti–Al system[12] as shown in Figure 1.2 in chapter 1. Ti_3Al and TiAl compounds can be formed by reducing the mixture of TiO_2 and Al_2O_3 with calcium as the reducing agent. Figure 3.1 represents the procedure of this study; raw material blending, high temperature reaction and acid leaching for removal of the by–product CaO.

3.2.1 Preparation of oxide mixture

For the preparation of oxide mixture, the following three methods were employed in this work:

3.2.1.1 Co–precipitation from chloride solution

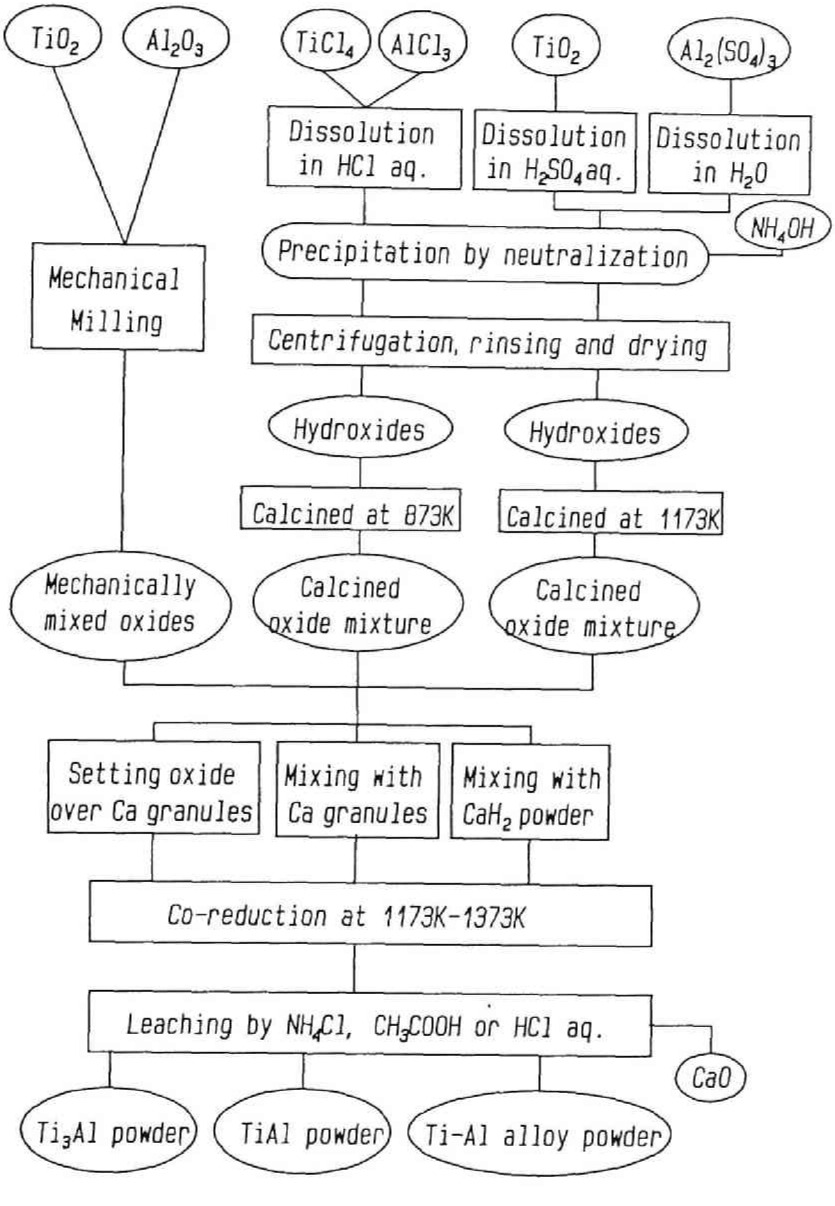


Figure 3.1: Experimental procedures.

High-purity $TiCl_4$ and $AlCl_3 \cdot 6H_2O$ were dissolved at a desired atomic ratio in concentrated HCl solution. This solution was dropped into aqueous ammonia solution to precipitate mixture of hydroxide of titanium and aluminum, and pH of the neutralized solution was controlled between 5 and 7[7]. After separation of the precipitates from the solution by centrifugation, the ammonium chloride adhering to the precipitates was removed by rinsing several times with distilled water. The white-colored cake of dried precipitate was ground into powder, and calcined at 873 K over night in air to evaporate NH_4Cl completely.

3.2.1.2 Co-precipitation from sulfate solution

TiO_2 was put in hot aqueous H_2SO_4 solution with $(NH_4)_2SO_4$, and dissolved into the solution. $Al_2(SO_4)_3$ was separately dissolved in water, and then mixed with the titanium ion containing solution. This blended solutions were added into ammonia solution and the simultaneous precipitates were rinsed, dried and calcined at 1173K in air for 10ks.

3.2.1.3 Mechanical mixing of oxide

The mechanical mixture was prepared by mixing rutile and α-alumina powder in a desired ratio using an agate mortar. The particle sizes of high purity TiO_2 and Al_2O_3 used here were in the order of sub-microns.

3.2.2 Reduction and leaching

Three possible kinds of reductant (vapor calcium, liquid calcium and solid CaH_2 powder) are applicable to the reduction of oxides. The choice was made after examination of all three cases. Both the calcium and CaH_2 used in this study were of about 98% purity: CaO was the main impurity.

The reduction experiments were carried out in a stainless steel vessel. In the case of reduction by calcium saturated vapor, the apparatus and experimental method have been described in the chapter 5 in Part II, and only a brief outline will be given here. The reducing agent was put on the bottom of the vessel, and the premixed oxide powders were placed on a molybdenum tray in the vessel. After a given holding time in the purified argon atmosphere at a reduction temperature between 1123K and 1373K, the vessel was cooled in a furnace. Equilibrium vapor pressure of calcium is evaluated to be 1750Pa at 1273K[11]. Special care was taken to avoid the leakage of the reductant from the vessel.

For the reduction by liquid calcium, the calcium metal granules were mixed with the oxide mixture and loaded on a molybdenum tray. For the reduction by CaH_2, 1.2 to 3.0 times the stoichiometric quantities of CaH_2 powder were well blended with the oxide mixture, compacted into a disk and inserted into a reduction vessel lined with molybdenum foil.

The reduction products containing the desired compound, CaO and the residual reducing agent often formed a hard cake especially when liquid calcium or CaH_2 was used. They were crushed and slurried in 1.53 mol kg^{-1} NH_4Cl, CH_3COOH (pH=3) or 1 kmol m^{-3} HCl aqueous solution with supersonic vibration or stirring. The centrifugated compound powders were rinsed with distilled water, alcohol and acetone, then dried in a vacuum.

3.2.3 Analysis of obtained compounds

The identification of the phases existing in the specimens was carried out by X-ray diffractometry using a Philips PW1700 system, and the results were compared with JCPDS cards. X-ray microprobe analysis (XMA, Hitachi X-650) was done to obtain the compositional profiles. The morphology and configuration of the powder were examined by scanning electron microscopy (SEM, Hitachi S-450) without etching and without electron-conductive evaporated film. A LECO TC336 analyzer was used for oxygen analysis, and calcium was chemically analyzed by both atomic absorption spectrometry (SIMADZU AA-670) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, Nippon Jarrell-Ash, ICAP-575II).

3.3 Results

3.3.1 Preparation of Ti_3Al

The calcined precipitates started from the chloride or sulfate were identified as the mixture of TiO_2 and Al_2O_3 by X–ray diffraction measurements. The specimens reduced by calcium vapor or calcium liquid consisted of the desired compound and the by–product, CaO. The excess reducing agent, calcium, also coexisted with them. These results agreed well with the work by Suzuki *et al.*[7]. Figure 3.2 shows the X–ray diffraction patterns of the samples reduced by CaH_2, where (a) and (b) show the reduction products and the compound powders after leaching, respectively. The metallic calcium was often found after reduction by CaH_2, while CaH_2 was hardly detected by X–ray diffraction measurements. CaO and calcium were easily removed by the wet method. In the case of the powders after reduction by calcium vapor, calcium liquid or CaH_2 and the subsequent leaching, X–ray diffraction measurements confirmed that the Ti_3Al single phase existed in all the specimens started from the oxide mixture containing Al_2O_3 and TiO_2 with a Al/Ti ratio of 1/3. From the view of identification of the formed phases, there was no difference between the specimens started from the calcined oxide mixtures and the mechanical oxide mixtures. No transient oxide phases were detected in the samples reduced for periods longer than 3.6ks, which was the shortest in this work. Ca–Al alloys as the by–product were never detected after the reduction.

Table 3.1 summarizes the analyses of calcium and oxygen concentrations in the reduced Ti_3Al powders. Three leaching solutions, aqueous NH_4Cl, CH_3COOH and HCl solutions, were used to dissolve the by–product CaO and the residual reducing agent, but no significant difference was recognized among them. The analyzed oxygen and calcium level in the Ti_3Al compound powders depended strongly on the experimental conditions. The oxygen concentrations of the powders reduced by vapor calcium or liquid calcium were about 2500–4000 mass ppm, which was higher than those by CaH_2 (about 1200–3000 mass ppm). From 73 independent experiments we obtained the lowest concentration of oxygen and calcium as 1200 mass ppm and 180 mass ppm, respectively.

To clarify the effect of oxygen dissolved in the washing solution, argon gas, air or pure oxygen gas was blown into the CH_3COOH solution before and during leaching. As seen in Table 3.2 three kinds of gases gave similar results. Stirring the solution by gas bubbling might have an effect on impurity elimination on the surface of the reduced powder.

The scanning electron micrographs in Figures 3.3, 3.4 and 3.5 revealed the morphology of the calciothermic reduced Ti_3Al powders. The fine isolated particles

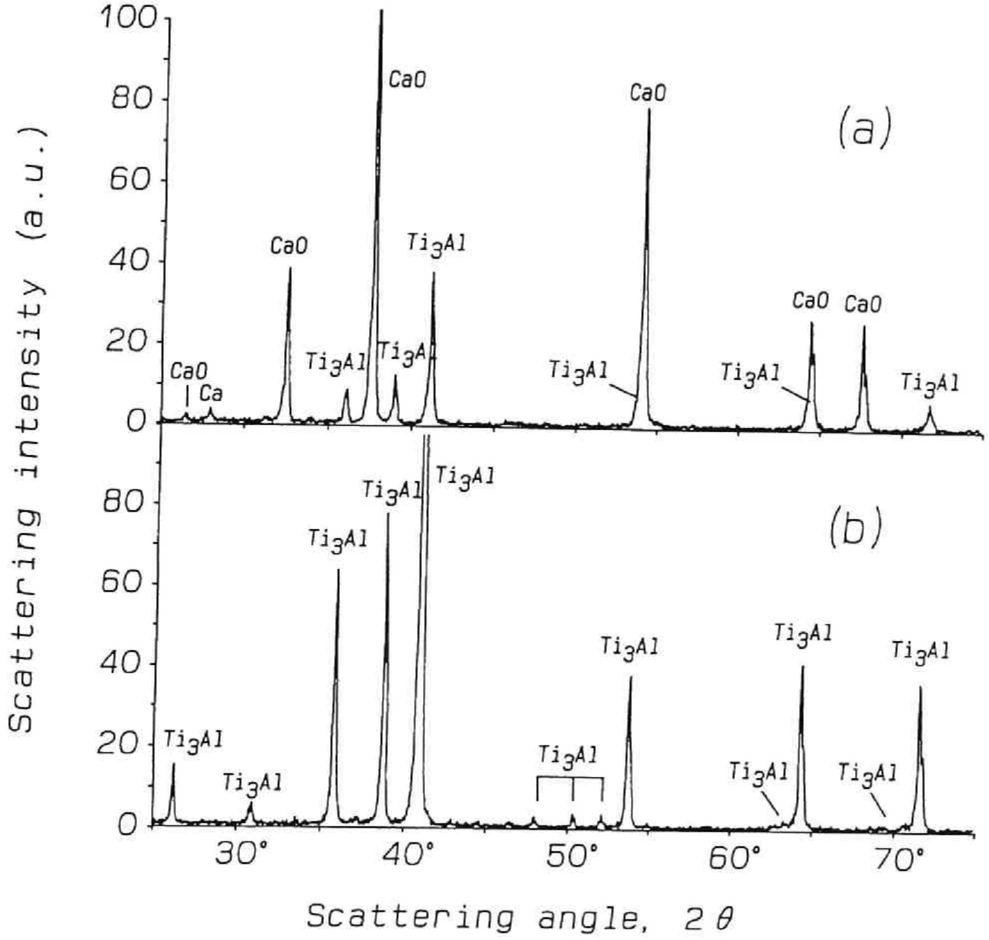


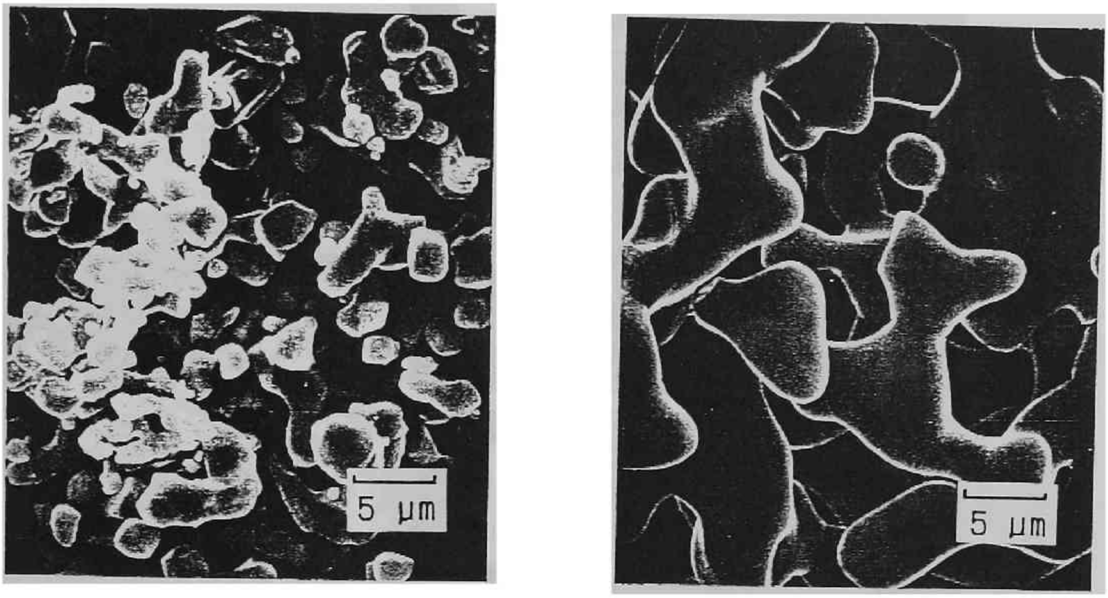
Figure 3.2: X-ray diffraction patterns using Cu $K\alpha_1$, of the Ti_3Al powder. The pattern (a) was for the specimen reduced at 1273K for 43.2ks by CaH_2, and the pattern (b) was for the same specimen after leaching of the reduced specimen with aqueous CH_3COOH solution.

Table 3.1: Results of chemical analysis of oxygen and calcium in the Ti_3Al specimens rinsed by aqueous NH_4Cl, CH_3COOH and HCl solutions.

Reducing	Leaching solution					
condition	CH_3COOH aq.		HCl aq.		NH_4Cl aq.	
1223 K	4600	ppmO	4300	ppmO	5600	ppmO
86.4 ks	1000	ppmCa	990	ppmCa	930	ppmCa
1273 K	2900	ppmO	3100	ppmO	—	
21.6 ks	830	ppmCa	1000	ppmCa	—	
1273 K	2500	ppmO	2500	ppmO	—	
21.6 ks	230	ppmCa	270	ppmCa	—	
1273 K	2500	ppmO	3500	ppmO	—	
21.6 ks	220	ppmCa	180	ppmCa	—	
1323 K	1600	ppmO	—		1200	ppmO
43.2 ks	2300	ppmCa	—		630	ppmCa

Table 3.2: Results of chemical analysis of oxygen and calcium in the Ti_3Al specimens after being reduced by CaH_2 and following leaching by aqueous CH_3COOH solutions for 14.4ks, where argon gas, oxygen gas and air was blown into the solutions during leaching.

Reducing	Leaching solution							
condition	Ar bubbling		Non bubbling		Air bubbling		O_2 bubbling	
1223 K	5400	ppmO	5800	ppmO	5900	ppmO	—	
43.2 ks	940	ppmCa	1000	ppmCa	1000	ppmCa	—	
1273 K	2900	ppmO	3700	ppmO	—		—	
21.6 ks	790	ppmCa	900	ppmCa	—		—	
1323 K	2400	ppmO	2200	ppmO	—		2300	ppmO
86.4 ks	300	ppmCa	450	ppmCa	—		340	ppmCa
1323 K	2200	ppmO	—		—		2000	ppmO
43.2 ks	390	ppmCa	—		—		460	ppmCa



(a) (b)

Figure 3.3: Scanning electron micrographs of Ti_3Al powders reduced by CaH_2 for 43.2 ks at 1223K(a) and 1323K(b), respectively. CaO was removed by leaching. The oxygen concentration of these powders were analyzed to be 4500 and 2600 mass ppm for (a) and (b), respectively.

could be seen after the removal of CaO. The particle size depended significantly on the reducing temperature, the reducing period and the reductant, but not on the history of the starting oxide mixture. The reduced powders were found to have a tendency to be sintered at higher temperatures or for longer periods, and to decrease their oxygen concentrations.

Titanium and aluminum atoms in the reduced powder were dispersed homogeneously within the limit of resolution of XMA. We could not detect any traces of chlorine or sulfur in the reduced specimens, which might have come from the starting chloride or sulfate[7] could not detected. Since the chemically analyzed aluminum concentration of the reduced Ti_3Al powder corresponded to the nominal concen-

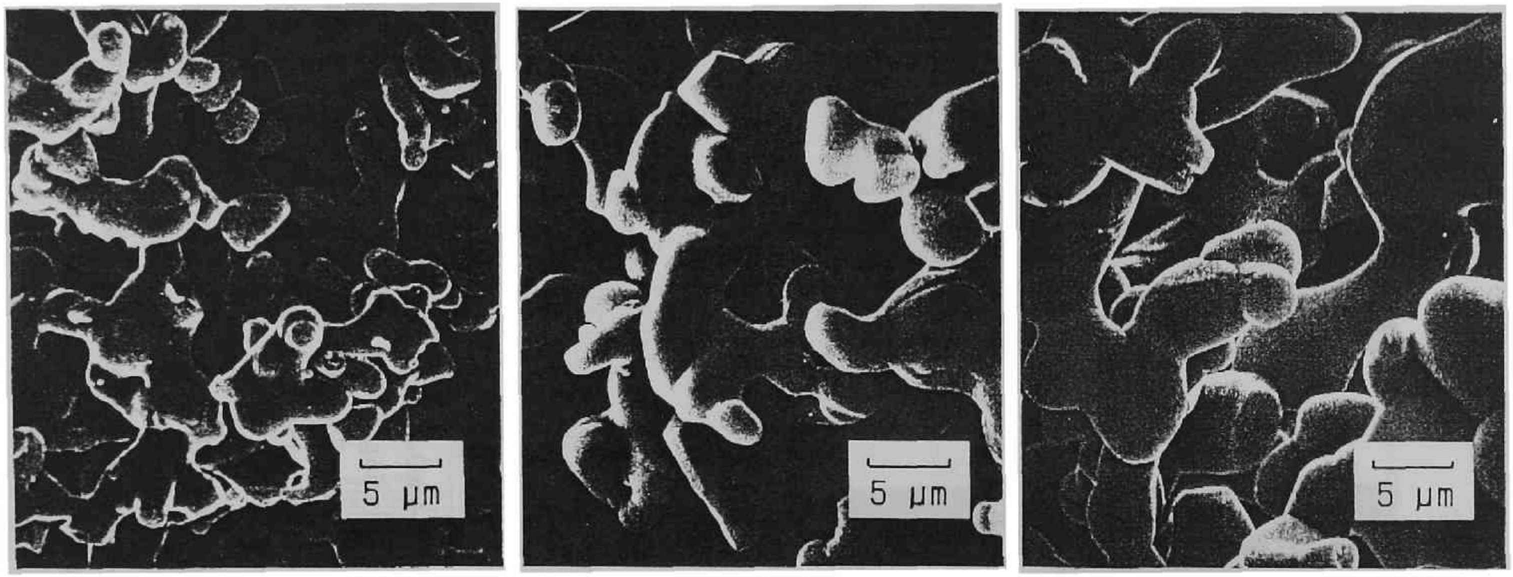
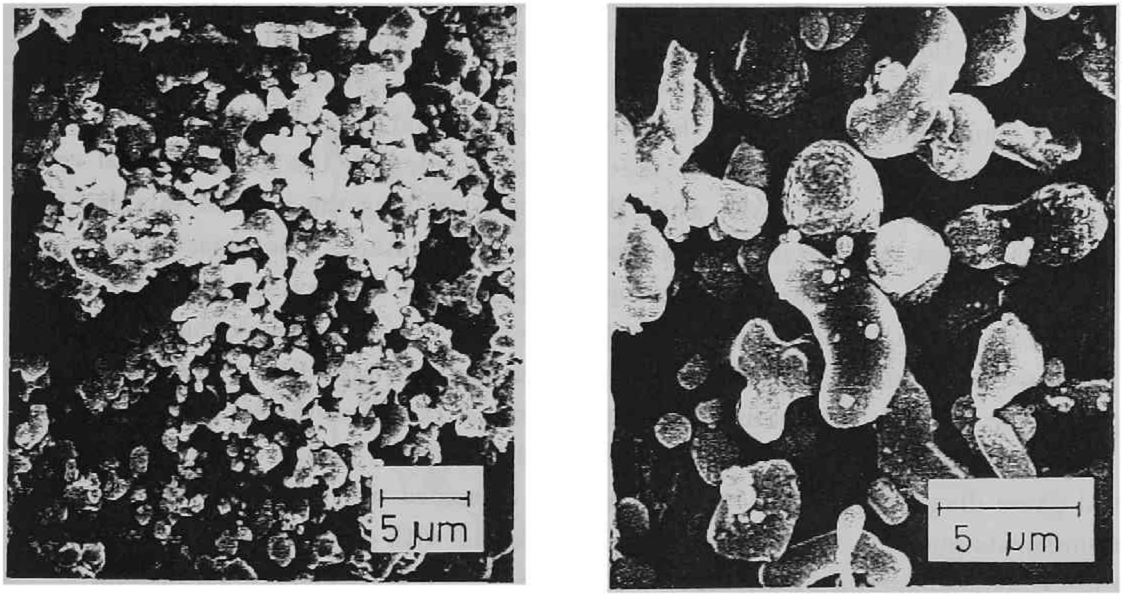


Figure 3.4: Scanning electron micrographs of Ti_3Al powders reduced by CaH_2 at 1273K for 10.8ks (a), for 43.2ks (b) and for 86.4ks (c). CaO was removed by leaching. The oxygen concentration of these powders were analyzed to be 2600, 2100 and 2100 ppm for (a), (b) and (c), respectively.



(a) (b)

Figure 3.5: Scanning electron micrographs of Ti_3Al powders reduced at 1273K for 10.8ks by calcium vapor (a) and calcium liquid (b). CaO was removed by leaching.

tration (25mol%Al) within the experimental error(±2mol%), as will be mentioned later, it is concluded that the obtained powder was consisted of homogeneous Ti_3Al intermetallic compound with the desired composition.

3.3.2 Preparation of hexagonal solid solution

After leaching, X–ray diffraction measurements for Ti–0 to 40 mol%Al powders confirmed that the hexagonal phase (α–Ti and Ti_3Al) existed in all the samples reduced at 1273 K for 3.6–180 ks. According to the phase diagram[12], Ti–Al alloys in a lower aluminum concentration than 8.6 mol%Al should have the high temperature structure, β–Ti, at 1273K, but the obtained powders in this compositional range showed still hexagonal even when the vessel containing the reduced sample was rapidly cooled into water from the reduction temperature. They must have, therefore, transformed into α–Ti during cooling. The lattice constants of the hexagonal α–Ti and Ti_3Al phases obtained by this co–reduction technique using CaH_2 were plotted in Figure 3.6 against the nominal aluminum composition of the starting oxide mixture. For comparison, the compositional ranges of the stable phases at 1273K are shown in the upper part of Figure 3.6, which is cited from the latest Ti–Al phase diagram[12]. The lattice constants coincided well with the previous measurements made on the bulk samples[13]–[16], and with our previous report of the co–reduction experiments by vapor calcium[7]. The measured lattice parameters decrease smoothly in each phase, showing that the powders obtained by this method have the same aluminum concentration as the bulk alloys.

Figure 3.7 shows the relationship between the nominal and analytical aluminum concentration of the reduced powders. The nominal compositions were fairly well maintained also in the final alloys although the data were somewhat scattered in the region of aluminum concentration more than 40 mol%Al, where Ti_3Al and TiAl coexist.

3.3.3 Preparation of TiAl

By using CaH_2 as the reducing agent, TiAl single phase was successfully produced after the reduction at 1273K for 10.8ks from either the calcined oxide mixture or the mechanically mixed oxides, which contained Ti and Al with the atomic ratio of 1:1. Ti–50mol%Al powder formed by this procedure was about 1μm in particle

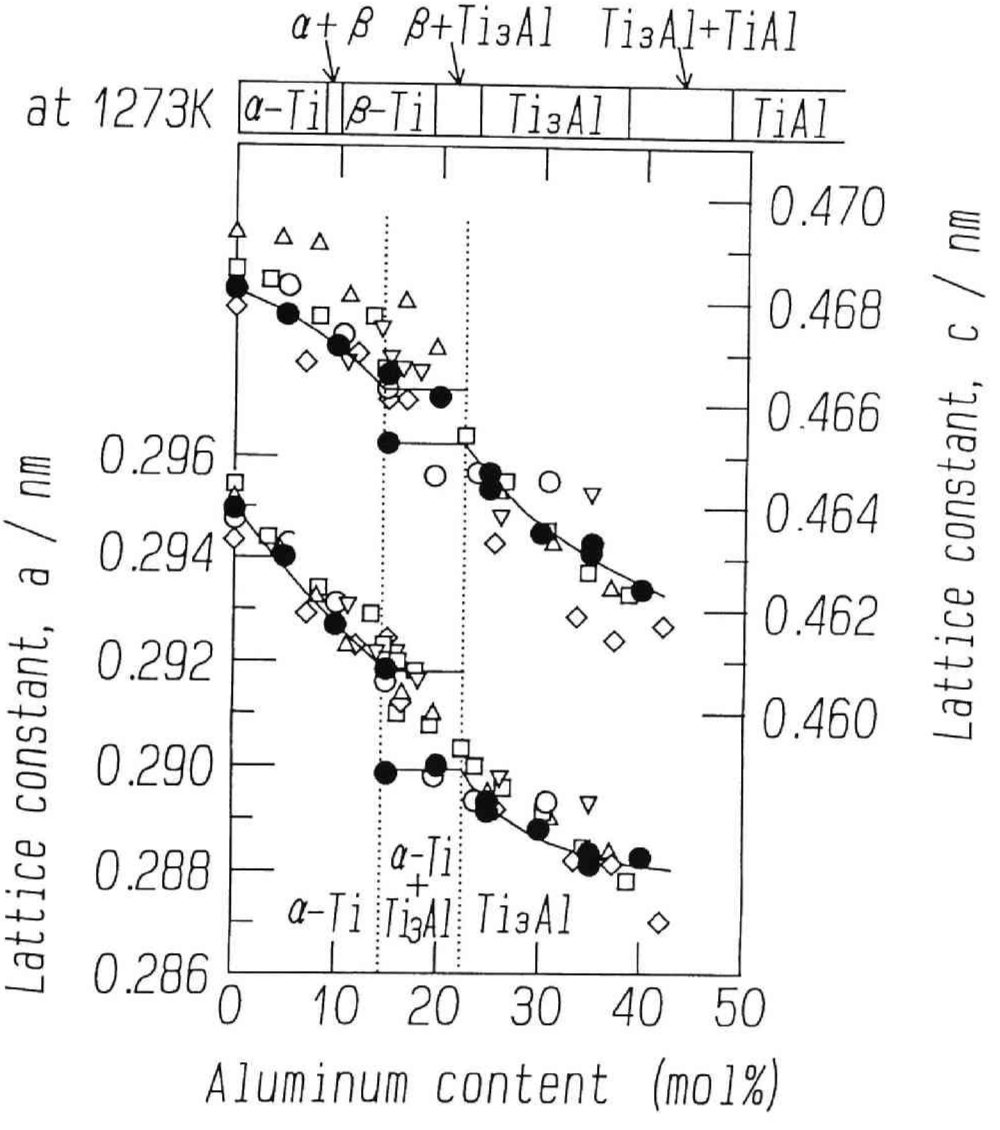


Figure 3.6: Lattice constants of the hexagonal phases after reduction by CaH_2 at 1273K for 43.2ks. The symbols in the figure are as follows; •: This study by CaH_2, o: Suzuki *et al.* by calcium vapor[7], △: Ogden et al.[13], ◇: Bumps *et al.*[14], □: Clark *et al.*[15] and ▽: Crossley[16].

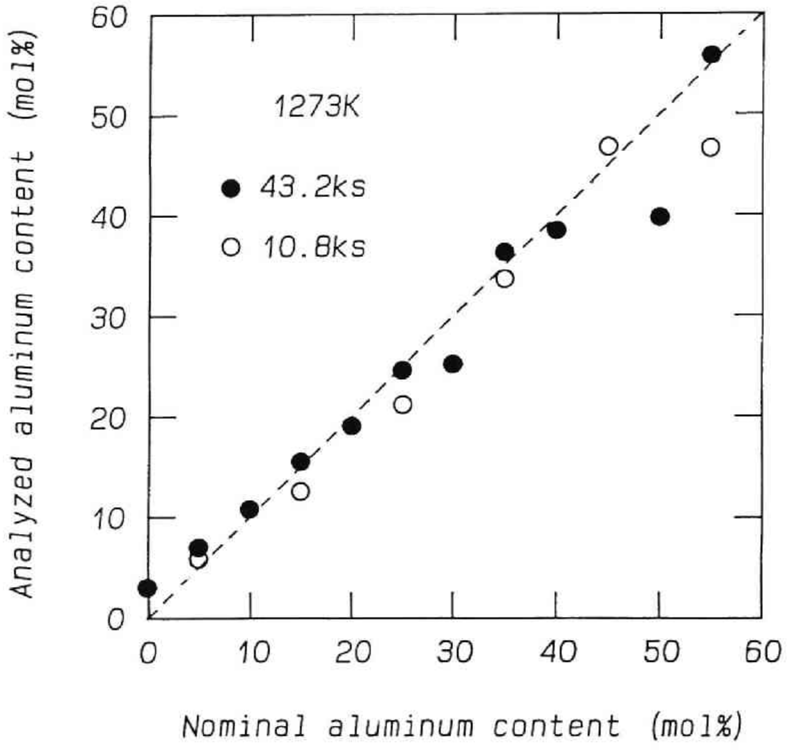


Figure 3.7: Analyzed aluminum concentration against the nominal aluminum compositions in the starting oxide mixture. The nominal compositions are shown as the ratio of Al/(Al+Ti). The open and closed circles show the analyzed values of the specimens reduced at 1273K for 10.8 ks and 43.2 ks.

size and contained about 3000 mass ppm oxygen and 1150 mass ppm calcium on an average of six independent runs.

For the reduction of the oxide mixture containing Ti and Al with the ratio of 1:1, however, Ti_3Al compound and $CaAl_2$ were preferentially produced in addition to TiAl, in both cases when the excessive amount of vapor calcium or liquid calcium was used and when the reduction time was longer than 10ks at 1273K. The same result has already been reported by Suzuki *et al.*[7]. For the powder reduced by using 1.2 to 2.0 times the stoichiometric amount of CaH_2, only TiAl was detected by the X-ray diffraction. However 3.0 times the stoichiometric amount produced the mixture of TiAl and Ti_3Al after the reduction and leaching. The evidence of the loss of aluminum atoms for the reduced powders were also shown in Figure 3.7. The formation of Ti_3Al coexisting with TiAl depended on the quantities of CaH_2, as mentioned above.

3.4 Discussion

3.4.1 Oxygen concentration in the reduced compound

Oxygen concentrations have been experimentally achieved to be 1000–2000 mass ppm for pure titanium as described in chapter 5 in part II, and 800–2400 mass ppm for Ti-6Al-4V alloy[17] by the calciothermic method using liquid calcium, although the theoretical deoxidation limit of oxygen concentration in titanium wire at 1273K is about 500 mass ppm, which has been achieved only from thermodynamic equilibrium among titanium, calcium, and calcium oxide as mentioned in chapter 1 in part II. Because of the lack of information about the solubility limit of oxygen in Ti_3Al and TiAl, and about their thermodynamic data for oxygen, it cannot be judged at this stage whether the oxygen concentration attained experimentally (1200 mass ppm at lowest) is reasonable. Figure 3.3 and 3.4 show that the oxygen concentration in the reduced Ti_3Al powders depends on the particle size. This means that the oxygen concentration is considerably affected by the re-oxidation on the surface of the fine particles occurred during handling in air after the reduction.

3.4.2 Calcium hydride as a reductant

CaH_2 has been considered to decompose completely into calcium and hydrogen gas below 1273K[18][19]. Therefore, CaH_2 may attack the oxide mixture as a form of vapor calcium or liquid calcium at the reduction temperature. CaH_2 powder could be blended with oxides better than calcium granules and located more closely near the oxide mixtures. Therefore, CaH_2 powder can have wider reaction area with the oxide mixture than calcium granules, and CaH_2 might be able to decrease the oxygen concentration in Ti_3Al more effectively than the vapor or liquid calcium.

The other thermodynamic data[11][20]–[22], however, show that CaH_2 does not decompose completely and a part of CaH_2 remains in its solid or liquid form even in the reduction temperature if the decomposed hydrogen gas does not escape from the vessel: the equilibrium hydrogen pressure at its melting temperature, 1273K[20], has been evaluated to be 29[20], 48[21] or 63 kPa[11][22]. Residual CaH_2 can contribute directly to the reduction of the oxides, and hydrogen gas is produced by the reaction.

Since the initial reductant, CaH_2, could not be found after the reduction, the former mechanism might be possible. But, it can not be strictly judged which mechanism operated as there is no other supporting evidences. No matter which mechanism takes place in the case when CaH_2 is used, however, hydrogen gas is produced during the reduction and it gives higher inner pressure in the reduction vessel: if the charged CaH_2 decomposed completely, for example, the hydrogen pressure would arrive to a few tens of MPa. Most of the hydrogen gas might leak out of the vessel from the gap between the vessel and the lid, or diffuse through the stainless steel wall, but this is not a serious problem for the reduction of oxides, because hydrogen gas with such pressures can thermodynamically reduce TiO_2 only to Ti_2O_3[20]. In this study, the stoichiometric amount of CaH_2 was calculated by neglecting the effect of hydrogen gas on the reduction of oxides.

3.4.3 Ti–Al–Ca phase diagram

The phase diagram of the Ti–Al–Ca system at 1273K shown in Figure 3.8, which is determined in chapter 1, shows that α–Ti and β–Ti are in equilibrium with almost pure liquid calcium, i.e. at maximum 1.1 mol%Al and 3.2mol%Al, respectively. But the region coexisting with Ti_3Al and TiAl is in equilibrium with the liquid Ca–20.2 mol%Al alloy, and TiAl single phase can coexist with the calcium liquid for a wide compositional range between 20.2 and 46.5 mol%Al at 1273K. Metallic titanium and Ti_3Al after the reduction are, therefore, equilibrated with Ca–dilute aluminum alloys, but the TiAl phase cannot be equilibrated with this Ca–dilute aluminum alloys. This is due to the fact that since an excessive amount of calcium is used for the reduction of these experiments because of the leakage of calcium vapor, the obtained TiAl powders lose aluminum after the reduction by producing Ca–Al alloys. This may be the reason why some analyzed aluminum concentration over 40 mol%Al were slightly lower than the nominal concentration as shown in Figure 3.7. In producing the TiAl phase by using liquid or vapor calcium, Ti_3Al and $CaAl_2$ were detected after the co–reduction. According to the phase equilibria mentioned above, $CaAl_2$ may be formed during solidification of aluminum rich calcium liquid alloy. When quite an excessive amount of CaH_2 was used for the preparation of TiAl, Ti_3Al was also detected in addition to TiAl. This suggests that neither CaH_2 nor hydrogen gas significantly change the phase equilibria shown in Figure 3.8 even if hydrogen lowers the activity of calcium when CaH_2 coexists with calcium[21]. TiAl might coexist, therefore, with Ti_3Al and Ca–Al liquid alloy containing about 20mol% aluminum when the amount of CaH_2 is excessive for the reduction. For further quantitative discussion, information about the Ti–Al–Ca–O–H system is required.

3.5 Conclusions

The clean and fine Ti_3Al and TiAl compound powders were produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using vapor calcium, liquid calcium or CaH_2.

This procedure consists of three steps: raw oxide blending, co–reduction and leaching. The methods for the preparation of the oxides mixtures had no effect on the production of the powders of a desired composition. The use of CaH_2 powder for the reduction gave better results than that of the other reductants on oxygen concentration in the reduced powders. The lowest oxygen and calcium levels in Ti_3Al powder were 1200 mass ppm and 180 mass ppm, respectively.

The indication on stoichiometric control in this procedure is thermodynamically discussed.

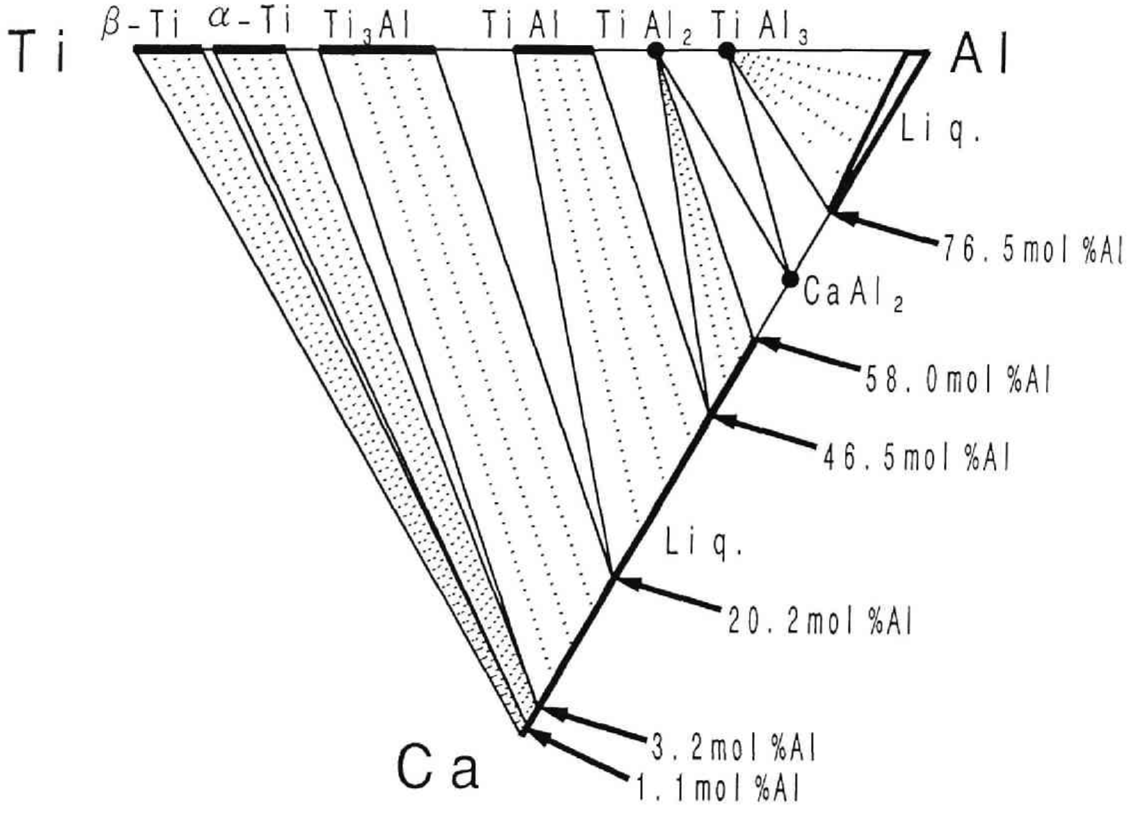


Figure 3.8: Phase diagram of the Ti–Al–Ca system at 1273K.

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Chapter 4

Preparation of $TiAl_3$ Powders by Calciothermic Reduction of Oxides

4.1 Introduction

Three kinds of titanium–aluminum intermetallic compounds, Ti_3Al, TiAl and $TiAl_3$, are of the extensive interest for the future structural materials. Because of their poor ductility, the clean and fine powders are required for the powder metallurgy of these compounds. The study described in chapter 2 showed that co–reduction of oxide mixtures using metallic calcium can produce the fine Ti_3Al and TiAl powders suitable for the powder metallurgy, since calciothermic reduction of oxides produces alloy powders at low temperatures without melting[1][2].

The purpose of this work is to establish experimentally the practical processes to prepare the fine $TiAl_3$ compound powders by the calciothermic reduction. The chemical reaction to produce $TiAl_3$ from oxides can be described by the equations:

$$2\ TiO_2 + 3\ Al_2O_3 + 13\ Ca = 2\ TiAl_3 + 13\ CaO \tag{4.1}$$

CaH_2 is available for the reduction of TiO_2 and Al_2O_3 and has been used to produce rare earth magnets[3][4], Ti_3Al and TiAl by the co–reduction. In chapter 3, it was reported that the hydrogen coming from calcium hydride did not affect any reactions in the Ti–Al system, and that CaH_2 was more effective than metallic calcium for the reduction of TiO_2. These reactions are characterized by starting from easily available oxides, but there are some difficulties relating to (1) removal of oxygen, (2) single phase preparation, and (3) stoichiometry control of the compounds[1][5][6].

At first glance, preparation of $TiAl_3$ single phase by the calciothermic reduction presents some difficulties. When Ca-Al alloys less than 75.6mol%Al were used as reductant, mingling of $TiAl_2$ and/or $CaAl_2$ is unavoidable during reduction as predicted from the results obtained in chapter 3 and the phase diagram of the Ti–Al–Ca system investigated in Figure 1.7 in chapter 1. Furthermore, the calculated phase diagram of the Ca–Al–O system at 1273K shown in Figure 1.10 in chapter 1 indicates that aluminum-rich Ca–Al alloys more than 87.8mol%Al are not suitable for reduction because it is easy to form by-product oxides such as $Ca_3Al_2O_6$ during reaction.

The objective of this study is to develop of an adequate process for producing the $TiAl_3$ single phase by the calciothermic reduction.

4.2 Experimental

Figure 4.1 represents the procedure of this work; raw material blending, high temperature reaction and acid leaching for removal of the by-products.

For the preparation of oxide mixture, rutile and α–alumina powder were mixed in a desired ratio using an agate mortar. The particle sizes of high purity TiO_2 and Al_2O_3 used here were in the order of sub-microns. CaH_2 used in this study was of about 98% purity: CaO was the main impurity. The CaH_2 powder was mixed with the oxide mixture by blending in advance.

The apparatus and experimental method for the reduction experiments were similar to those described in previous chapters. About 1g of the premixed powder sample was placed on the molybdenum tray, and they were tightly covered with a stainless steel cap and a bottom plate. Special care was taken to avoid the leakage of the reductant from the vessel. After a given holding time in the purified argon atmosphere at 1273K or 1373K, the vessel was cooled in the furnace.

The reduction products containing the desired compound, CaO and the residual reducing agent often formed a gray-colored hard cake with about 10 mm in diameter and about 3 mm thick. They were crushed and slurried in CH_3COOH aqueous solution (pH=3). The successive leaching by 1 kmol m^{-3} HCl aqueous solution was done with supersonic vibration. The centrifugated compound powders were rinsed

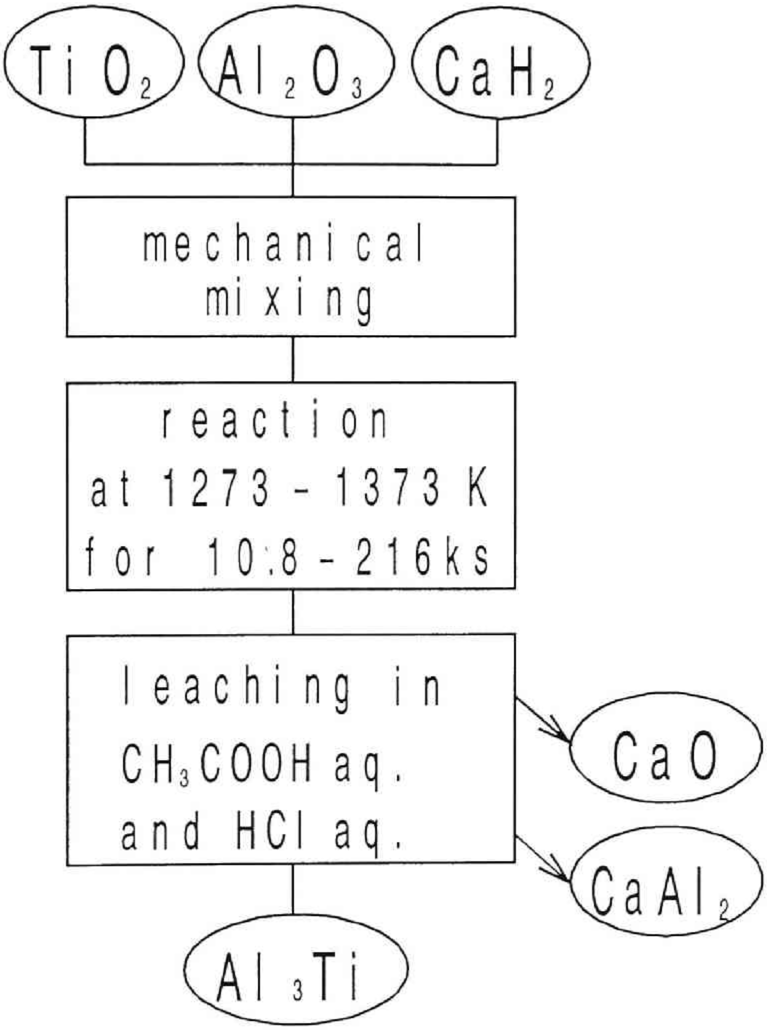

Figure 4.1: Experimental procedures.

with distilled water, alcohol and acetone, then dried in a vacuum.

The identification of the phases existing in the samples was carried out by X-ray diffractometry, and the results were compared with JCPDS cards and the reported data of $TiAl_2$[7]. X-ray microprobe analysis (XMA, Hitachi X-650) was done to obtain the compositional profiles. The morphology and configuration of the powder were examined by scanning electron microscopy (SEM, Hitachi S-450). A LECO TC336 analyzer was used for oxygen analysis. Aluminum and calcium were chemically analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Nippon Jarrell-Ash ICAP-575II).

4.3 Results and Discussion

4.3.1 Preparation of $TiAl_3$

Figure 4.2 shows X-ray diffraction (XRD) patterns of the sample reduced by CaH_2 at 1273K for 10.8ks. The starting material was the oxide mixture containing Al_2O_3 and TiO_2 with a Al/Ti ratio of 3/1. The pattern (a) shows that the sample after the reduction contained CaO and $Ca(OH)_2$ as the major phases. $Ca(OH)_2$ seems to be formed by the reaction of CaO with the atmospheric moisture during handling before XRD measurement. The metallic calcium and CaH_2 were hardly detected by X-ray diffraction for all the specimens studied here. CaO and $Ca(OH)_2$ were easily removed by CH_3COOH aq. as shown in Figure 4.2 (b), where the existence of $CaAl_2$ and $TiAl_2$ in addition to $TiAl_3$ is more clearly seen than in Figure 4.2 (a). The by-product, $CaAl_2$, could be completely separated after leaching by HCl aqueous solution. The powder containing $TiAl_3$ and $TiAl_2$ were obtained as shown in Figure 4.2 (c).

When the stoichiometric amount of CaH_2 was used for the reduction of the oxide mixture containing Ti and Al at the ratio of 1:3, a large amount of complex oxides in the Ca-Al-O system such as $Ca_{12}Al_{14}O_{33}$ was produced in addition to $TiAl_3$ even after the reduction time longer than 10ks at 1273K. The amount of reductant was, therefore, increased to 1.2 times the stoichiometric amount as shown in Figure 4.2. The complex oxides could not be detected in this case, but the by-product, $CaAl_2$, was formed by the excess amount of calcium. $TiAl_2$ and $CaAl_2$ were preferentially

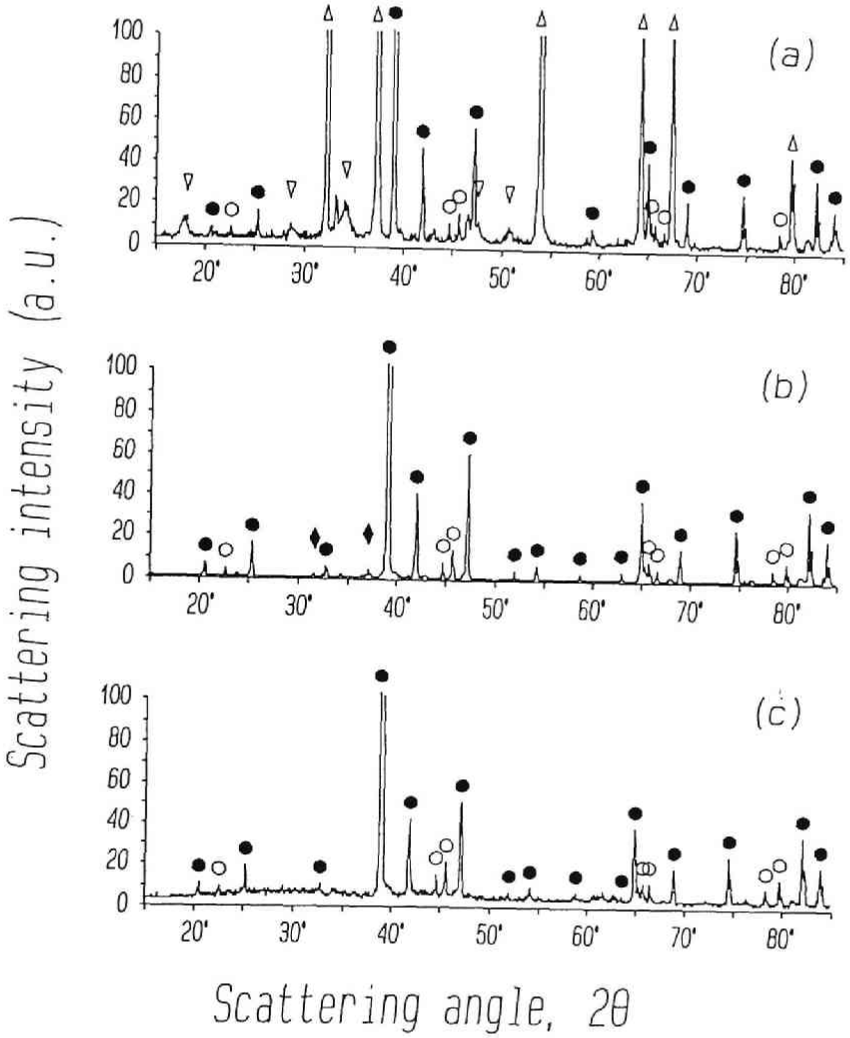

Figure 4.2: XRD patterns using CuK_α for the sample reduced at 1273K for 10.8ks from the oxide mixture with a ratio of Al/Ti = 3/1. Pattern (a) was for the as-reduced specimen. (b) was for the same specimen after leaching in CH_3COOH aqueous solution. (c) was for the same specimen after the subsequent leaching in HCl aq. The symbols in the figure indicate CaO(△), $Ca(OH)_2$(▽), $CaAl_2$(◆), $TiAl_2$(○) and $TiAl_3$(●).

Table 4.1: The results of the phase identification by XRD measurement and XMA for the samples reduced from the oxide mixtures with the various compositions. The co–products were determined for the samples after the reduction at 1273K for 10.8ks and also after the subsequent leaching by CH_3COOH aq.

Molar ratio in the oxide mixture Ti : Al	Identified phases					
	Al–Ti alloys			Co–products		
35 : 65	TiAl,	$TiAl_2$		CaO,	$CaAl_2$	
30 : 70		$TiAl_2$,	$TiAl_3$	CaO,	$CaAl_2$,	$Ca_3Al_2O_6{}^*$
25 : 75		$TiAl_2$,	$TiAl_3$	CaO,	$CaAl_2$	
20 : 80			$TiAl_3$	CaO,	$CaAl_2^*$	
15 : 85			$TiAl_3$	CaO,	$CaAl_2$,	$Ca_{12}Al_{14}O_{33}^*$
10 : 90			$TiAl_3$	CaO,	$CaAl_2$,	$Ca_{12}Al_{14}O_{33}$
0 :100		—		CaO,	$CaAl_2$,	$Ca_{12}Al_{14}O_{33}$

* : Minor phase in the specimen.

produced in addition to $TiAl_3$, both when the excessive amount of CaH_2 was used and when the reduction was made for longer than 10ks at 1273K. The similar results have already been shown in the preparation of TiAl in the previous chapter.

It was thought that the formation of $CaAl_2$ decreased aluminum concentration of Al–Ti alloy in the sample, and that $TiAl_2$ was, therefore, formed in addition to $TiAl_3$. It was needed to increase the Al/Ti ratio in the oxide mixture larger than 3/1 in order to compensate the aluminum loss. The excess amount of CaH_2 was needed both for the complete reduction of oxides and for the lack of calcium due to a small amount of leakage from the vessel. An gas tight vessel, for example, sealed by welding, may give a better result. In this study 1.2 to 1.8 times the stoichiometric amount of CaH_2 was normally used for the reduction.

Table 4.1 summarizes the results of the phase identification by XRD measurements and XMA for the samples reduced from the oxide mixtures with the various compositions. At the lower aluminum concentration than 75mol%Al, TiAl or $TiAl_3$ was produced in addition to $TiAl_2$. The formation of these two phase mixtures can be generally understood on the base of the phase diagram in Ti–Al binary system[8], although a small amount of $CaAl_2$ and $Ca_3Al_2O_6$ co–existed.

At the aluminum concentration range between 80 and 90mol%Al, $TiAl_3$ was ob-

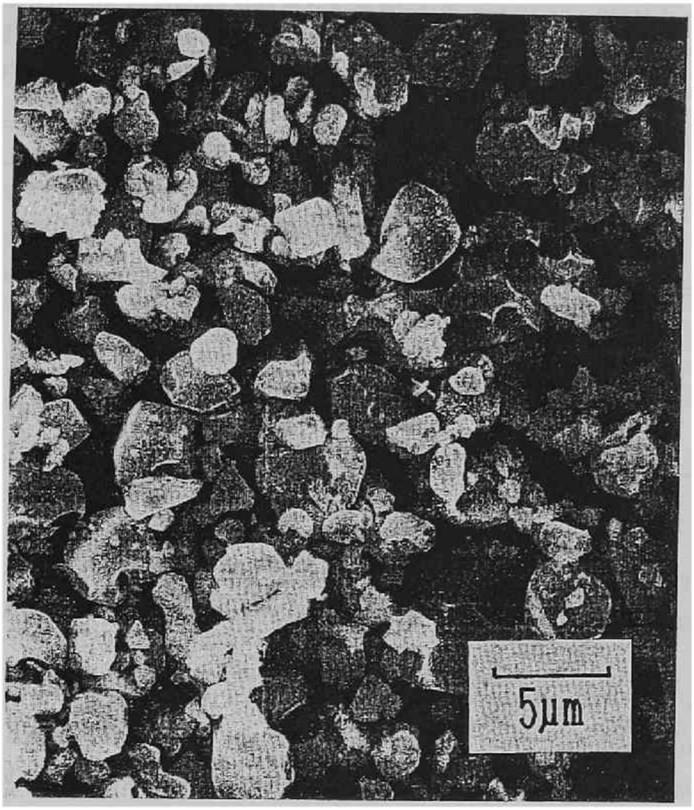

Figure 4.3: Scanning electron micrograph of TiAl$_3$ powders reduced by CaH$_2$ for 10.8 ks at 1273K. The molar ratio of Al:Ti in the starting oxide mixture was 85:15.

tained as the prevailing phase in the powder after the reduction at 1273K for 10.8ks. The samples in these compositions contained CaO, CaAl$_2$ and a very small amount of Ca$_{12}$Al$_{14}$O$_{33}$ as by–products of the reduction, and they could be separated by leaching. The scanning electron micrograph in Figure 4.3 revealed the morphology of the calciothermic TiAl$_3$ powder after the reduction of the oxide mixture in a ratio of Al/Ti=85/15. The fine isolated particles could be seen after the removal of CaO and the by–products. This powder contained about 2500 mass ppm oxygen and 350 ppm calcium on the average of three independent runs.

When pure alumina was reduced, as listed in Table 4.1, CaO, CaAl$_2$ and Ca$_{12}$Al$_{14}$O$_{33}$ were formed as the major phases and pure aluminum has rarely de-

Table 4.2: The results of the phase identification by XRD measurement and XMA for the samples reduced from the oxide mixtures with the various compositions. The co–products were determined for the samples after the reduction at 1273K for the period longer than 10.8ks and also after the subsequent leaching by CH_3COOH aq.

Molar ratio in the oxide mixture Ti : Al	Reduction time (ks)	Identified phases			
		Al–Ti alloys			Co–products
35 : 65	172.8	TiAl,	$TiAl_2$		CaO, $CaAl_2$
25 : 75	86.4	TiAl,	$TiAl_2$		CaO, $CaAl_2$
20 : 80	86.4		$TiAl_2$		CaO, $CaAl_2$
15 : 85	86.4			$TiAl_3$	CaO, $CaAl_2$
10 : 90	216			$TiAl_3$	CaO, $CaAl_2$

tected by the reduction of CaH_2. One of the reasons is that the molybdenum or tantalum plate holding the sample powder partially reacted with the produced aluminum.

In this work, the transient oxides, such as $Ca_3Al_2O_6$ and $Ca_{12}Al_{14}O_{33}$, disappeared after the prolonged reaction period or when the amount of CaH_2 was increased. Under the cases listed in Table 4.2, there were some changes in the phases obtained after leaching, compared with the results in Table 4.1. The phases with the lower aluminum content than that of initial composition were generally obtained in the conditions of Table 4.2. This was also confirmed by the chemical analysis that the aluminum concentration of the powders in the Al–Ti system decreased after the reduction. The reduction at 1373K gave the similar results as that at 1273K, as described above.

4.3.2 Processes of the calciothermic reduction

The phase diagram of Ti–Al–Ca system is a useful guide to explain the process to prepare Ti_3Al and TiAl by the calciothermic reduction as shown in the previous chapter. Supposing that Al_2O_3 and TiO_2 are independently reduced to the metallic state and then aluminum and titanium form the intermetallic compound, the phase diagram of the Ti–Al–Ca system investigated in chapter 1 gives us some significant

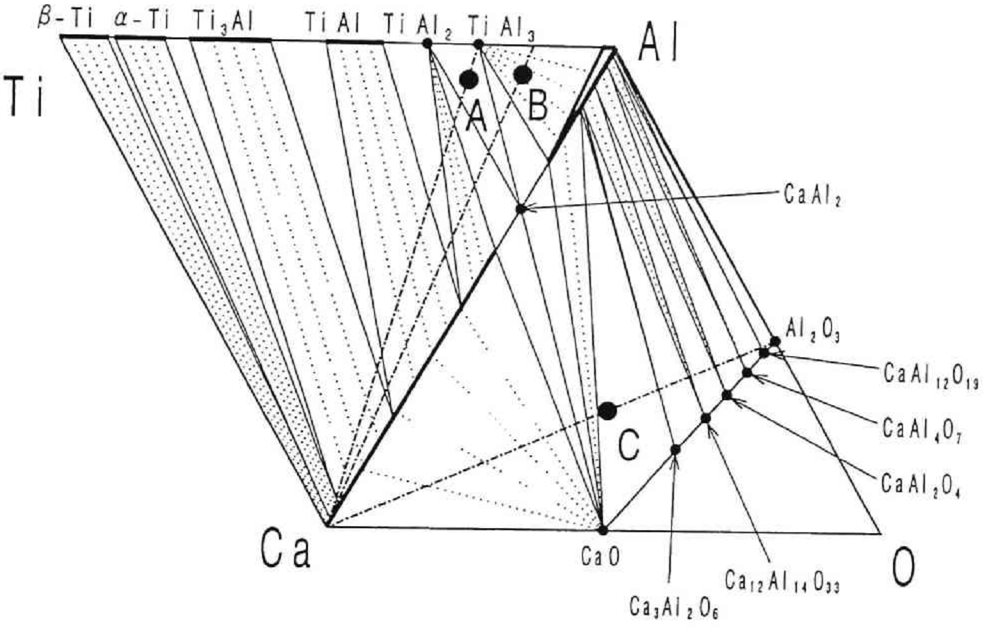

Figure 4.4: Explanation of the compositional change in the phase diagrams during the reduction

information why $CaAl_2$ was formed as the by–product.

$TiAl_3$ formed by the calciothermic reduction reacts with the excessive amount of calcium and the total composition of the system shifts from $TiAl_3$ to the point "A" in Figure 4.4, where $TiAl_2$ and $CaAl_2$ coexist with $TiAl_3$. This is the reason why the mixture of $TiAl_2$ and $TiAl_3$ was obtained from the oxide mixture with the compositional ratio of $Al/Ti=3$.

When the initial composition of the starting oxide mixture is controlled to be $Al/Ti>3$, for example, the point "B" in Figure 4.4, the reaction with calcium produces the Al–rich liquid in addition to $TiAl_3$. During cooling, the liquid may decompose into $CaAl_2$ and a small amount of aluminum or $CaAl_4$[9] ($CaAl_4$ is stable below

973K). The latter two phases, however, were not detected in this study, because they dissolve easily in acid solution during leaching.

The reduction process of Al_2O_3 are also shown in Figure 4.4, where many transient oxides may form with calcium on the way to Ca–Al alloy. If the stoichiometric amount of calcium for the reduction of Al_2O_3 is used (point "C" in Figure 4.4), the obtained phases should consist of three phases, liquid alloy with 87.8mol%Al, $Ca_3Al_2O_6$ and CaO. The Al–Ca liquid solidifies into $CaAl_4$ and aluminum according to the binary diagram[9]. The coexistence of CaO, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ was, however, found in this work. The reduction seems to be done through a non-equilibrium process. For further quantitative discussion to clarify the reduction route, the phase equilibria in the Ti–Al–Ca–O quaternary system are required.

In order to obtain the single phase of $TiAl_3$ in this stage, the compositional ratio in the oxide mixture and the amount of the reductant are important, because $TiAl_2$ as the by-product could not be removed by leaching in the acid solution. The oxides should be, therefore, mixed at the molar ratio of Al/Ti>3. The excessive amount of the reductant should be minimized so that the total composition does not enter the stable region of $TiAl_2$. The quantities of aluminum, titanium and calcium should be, therefore, controlled as the following three mass balances.

$$n_{\mathrm{Al}} \geq 3n_{\mathrm{Ti}} \tag{4.2}$$

$$n_{\mathrm{Ca}} \geq \frac{3}{2}n_{\mathrm{Al}} + 2n_{\mathrm{Ti}} \tag{4.3}$$

$$n_{\mathrm{Ca}} \leq 2n_{\mathrm{Al}} + \frac{1}{2}n_{\mathrm{Ti}} \tag{4.4}$$

where n_{Al} and n_{Ti} are the number of moles of aluminum and titanium, respectively. n_{Ca} is the total number of moles of metallic calcium and calcium in CaH_2 as a reductant in the vessel. In this condition, the co-product is only $CaAl_2$, CaO and aluminum-rich Ca–Al alloys, and $TiAl_2$ is not produced. These co-products are, therefore, easily removed by HCl aqueous solution.

4.4 Conclusions

The fine $TiAl_3$ compound powder was produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using CaH_2.

This procedure consists of three steps: raw oxide blending, co-reduction and leaching. After the reduction of the oxide mixture with the various compositions, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ were often formed as the by-product and transient oxide, respectively. The transient phases such as $Ca_{12}Al_{14}O_{33}$ and $Ca_3Al_2O_6$ were disappeared by the reaction for longer period than 10ks at 1273K. $CaAl_2$ as the by-product could be removed by leaching in HCl aqueous solution, but $TiAl_2$ could not. The obtained $TiAl_3$ powders were a few micrometer in particle size and contained about 2500 mass ppm oxygen.

Based on the phase diagrams of the Ti–Al–Ca and Ca–Al–O system at 1273K, $TiAl_3$ single phase in this calciothermic process could be produced by the strict control of the compositions of the oxide mixture and the amount of the reductant.

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Part IV

Summary

a. Summary

This investigation aims at to clarifying the thermodynamic properties of oxygen in dilute titanium–oxygen solid solution with the scope of discussing the feasibility of producing extra–low–oxygen titanium. Using these knowledge, the author developed some processes for direct reduction and deoxidation of titanium and Ti–Al intermetallic compounds.

In chapter 1 of part II, thermodynamic properties of dilute titanium–oxygen solid solution in β field was investigated. Oxygen activities of β–titanium–oxygen alloys were determined by equilibrating titanium–oxygen alloys with calcium and CaO at temperatures between 1173K and 1373K. From the analyzed oxygen concentration in titanium, the partial molar free energies of formation of oxygen in β–titanium were calculated by using the standard free energy of formation of CaO.

In chapter 2 of part II, and advanced deoxidation method was examined to attain the lower oxygen level. Some halide fluxes were tried in this study with the purpose of decreasing CaO activity. Several factors in choosing a flux and the process parameters for deoxidation were considered, and feasibility to produce extra–low–oxygen titanium was examined. Titanium wires and small pieces containing several hundreds mass ppmO were deoxidized to a level of a few tens mass ppmO by using $CaCl_2$ flux at 1273K. The oxygen sources to make worse the efficiency of the further deoxidation of titanium were discussed, and one of them was suggested to be the oxygen contamination in the flux. CaO contamination due to calcium reductant and adsorbed water on the surface of calcium and $CaCl_2$ were minimized by using calcium vapor and by flux pre–treatment. Ca–$BaCl_2$ and Ca–$CaCl_2$–Y_2O_3 fluxes were found to be less effective than $CaCl_2$ flux for deoxidation of titanium.

In chapter 3 of part II, characterization of extra–low–oxygen titanium was carried

out using high purity titanium deoxidized to a level of 20 – 60 mass ppm oxygen by use of Ca–$CaCl_2$ flux at 1273K. Trace element analysis, micro Vickers hardness measurements, and electrical resistivity measurements were made. The micro Vickers hardness value of electrolytically refined titanium was 80–90 kg/mm^2 following deoxidation. Resistivity measurements were carried out at 4.2, 77 and 298K on titanium wires. Deviation from Matthiessen's rule was observed for titanium samples with high residual resistivity. By deoxidizing electrolytically refined high purity titanium wire, titanium with a high residual resistivity ratio ($\rho_{298}/\rho_{4.2} \simeq 100$) was produced, and the ideal resistivities at 77 and 298K were determined to be 40 and 440 nΩm, respectively. The contribution by oxygen to resistivity at 4.2K was also measured by using titanium samples containing 30 and 500 mass ppmO, and determined to be 88 nΩm/mol%O.

In chapter 4 of part II, as an alternate method for deoxidation, electrochemical deoxidation of titanium was examined with the purpose of obtaining oxygen–free–titanium. Removal of oxygen in titanium using an electrochemical technique was examined at temperatures around 1223K. By applying more than 2.5V between titanium and carbon electrodes immersed in molten $CaCl_2$, titanium cathode samples were deoxidized. This is believed that the calcium activity increased and the CaO activity decreased around the titanium cathode surface. Titanium wires containing 1400 mass ppm oxygen were deoxidized to less than 100 mass ppm. In some cases, the oxygen concentration in titanium was lowered to below the detection limit(<10 mass ppm) of the conventional inert gas fusion analysis, whereas the carbon concentration was increased to about 50 mass ppm. The effect of applied voltage on oxygen, nitrogen and carbon concentrations in titanium was also investigated, and 2.8V was found to be the optimum for deoxidation. In the production of oxygen–free–titanium, the behavior of metallic contaminants was investigated using electrolytically refined high–purity–titanium as starting material.

In chapter 5 of part II, some attempts for producing titanium powders by direct reduction of titanium oxides were made. Clean and fine titanium powders were produced directly from the TiO_2 powders by the calciothermic reduction at 1273K using calcium granules or CaH_2 powders. By using CaH_2 as a reductant, the titanium powders containing about 1500 mass ppm oxygen were obtained after the removal of residual calcium and by–product CaO by leaching. The use of $CaCl_2$ flux gave better result on the oxygen concentration in the reduced powder, and powders containing about 1100 mass ppm was produced.

In part III, with the scope of developing effective process to produce clean and fine titanium aluminide powders, a fundamental study on refining of titanium aluminides was carried out. Several findings and knowledge obtained during the investigation of refining of titanium were applied for refining of titanium aluminide powders on the base of the thermodynamic consideration of the Ti–Al–Ca system at the reaction temperatures. The author developed effective methods for direct reduction of titanium aluminide powders from oxides. Deoxidation of titanium aluminides were also carried out with the purpose of producing extra-low-oxygen titanium aluminide powders.

In chapter 1 of part III, prior to the calciothermic reduction and deoxidation investigation, study on phase equilibria of the Ti–Al–Ca system at 1273K was conducted to determine the compositions of Ca–Al alloys used as deoxidant or reductant suitable for the calciothermic reduction and deoxidation to produce titanium aluminide powders. Based on these experimental phase equilibria and on the reported thermodynamic data in Al–Ca system, aluminum activities in the two phase regions in the Ti–Al system at 1273K were estimated. Using these values, titanium activities of the Ti–Al system at 1273K were calculated by Gibbs–Duhem integration, and standard free energies of formation of titanium aluminides were calculated at 1273K.

In chapter 2 of part III, removal of oxygen in titanium aluminide (TiAl) by the reaction with chemically active calcium–aluminum alloy was carried out around 1373K with the purpose of obtaining extra-low-oxygen TiAl. In experiments in which Ti–Al samples were submerged in liquid Ca–Al alloys at 1373K, the surface of the samples was severely deteriorated and became nodular. To prevent this surface deterioration, Ca–Al alloy deoxidant was, in most cases, supplied to the TiAl samples in vapor form. When TiAl powder was mixed with CaO, and the deoxidant was supplied in vapor form, powders initially containing 510, 1100 and 4200 ppmO were deoxidized to about 160, 490 and 670 ppmO, respectively, after deoxidation at 1373K for 86.4ks. Among many conditions tested, utilization of TiAl powders mixed with $CaCl_2$ proved to be the most effective for deoxidation at 1373K. $CaCl_2$ was used as a flux to facilitate the deoxidation by decreasing the activity of the reaction product CaO. TiAl powders mixed with $CaCl_2$ and reacted with Ca–Al vapor at 1373K for 86.4ks, were deoxidized to levels of 62, 140 and 190 mass ppmO from initial concentrations of 510, 1100 and 4200 mass ppmO, respectively. No significant change in morphology of the particle was observed after deoxidation. The titanium and nitrogen concentrations of the powders remained unchanged, whereas calcium, initially present in trace amounts, increased to 160 mass ppm by the deoxidation treatment.

In chapter 3 of part III, study on preparation of TiAl and Ti_3Al powders by calciothermic reduction of oxides was carried out at 1273K. Clean and fine Ti_3Al and TiAl compound powders were produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using vapor calcium, liquid calcium or CaH_2. The use of CaH_2 powder for the reduction gave better results than that of the other reductants on oxygen concentration in the reduced powders. The lowest impurities in the Ti_3Al powder were 1200 mass ppm oxygen and 180 ppm calcium. The indication on stoichiometric control in this procedure is thermodynamically discussed.

In chapter 4 of part III, fine $TiAl_3$ compound powder was produced directly from the oxide mixtures of TiO_2 and Al_2O_3 by calciothermic reduction using CaH_2. After the reduction of the oxide mixture with the various compositions, $CaAl_2$ and $Ca_{12}Al_{14}O_{33}$ were often formed as the by–product and transient oxide, respectively. The transient phases such as $Ca_{12}Al_{14}O_{33}$ and $Ca_3Al_2O_6$ were disappeared by the reaction for longer period than 10ks at 1273K. $CaAl_2$ as the by–product could be removed by leaching in HCl aqueous solution. The obtained $TiAl_3$ powders was a few micrometers in particle size and contained about 2500 mass ppm oxygen. Based on the phase diagrams of the Ti–Al–Ca and Ca–Al–O system at 1273K, a process to produce $TiAl_3$ single phase by this calciothermic reduction is established.

In conclusion, a fundamental study on refining of titanium and titanium aluminides was carried out to develop an effective method to produce high purity titanium and titanium aluminide powders on the basis of thermodynamic study on the Ti–O and Ti–Al–Ca systems at reaction temperatures.

It is believed that the knowledge and the findings obtained in this fundamental study would be helpful in development of titanium refining in future.

b. List of Publications

The main parts of this thesis are constructed from the following papers.

Chapter 1 in Part II

1. *Materials Transaction, JIM*, vol.32 no.5 (1991), pp.485–488.
   "Thermodynamic Properties of Dilute Titanium–Oxygen Solid Solution in Beta Phase",
   T.H.Okabe, R.O.Suzuki, T.Oishi and K.Ono

Chapter 2 in Part II

2. *Tetsu-to-Hagane (Journal of the Iron and Steel Institute of Japan)*, vol.77 no.1 (1991), pp.93–99.
   "Production of Extra Low Oxygen Titanium by Calcium–Halide Flux Deoxidation" (in Japanese)
   T.H.Okabe, R.O.Suzuki, T.Oishi and K.Ono:
3. *Proceedings of the International Conference on Titanium Products and Applications*, Florida, 1 – 5 Oct.(1990), pp.822–829.
   "Preparation of Extra Low Oxygen Titanium by the Calcium–Halide Flux Deoxidation Process"
   T.H.Okabe, R.O.Suzuki, T.Oishi and K.Ono

Chapter 3 in Part II

4. *Journal of Alloys and Compound (formerly Journal of the Less Common Metals)*, 184 (1992) pp.43–56.

"Preparation and Characterization of Extra–Low–Oxygen Titanium"
T.H.Okabe, T.Oishi and K.Ono

5. To be published on : *Proceedings of the 7th World Conference on Titanium*, San Diego June 28 – July 2 (1992).
   "Preparation and Characterization of Extra–Low–Oxygen–Titanium"
   T.H.Okabe, M.Nakamura, T.Ueki, T.Oishi and K.Ono

Chapter 4 in Part II

6. To be published on *Metallurgical Transactions* (May 1992)
   "Electrochemical Deoxidation of Titanium"
   T.H.Okabe, M.Nakamura, T.Oishi and K.Ono
7. *Journal of the Japan Institute of Metals*, vol.31 no.4 (1992) pp.315–317.
   "Production of Extra Low Oxygen Titanium by Calcium–Halide Flux Deoxidation"
   T.H.Okabe, M.Nakamura, T.Ueki, T.Oishi and K.Ono

Chapter 5 in Part II

8. *Tetsu–to–Hagane (Journal of the Iron and Steel Institute of Japan)*, vol.76 no.4 (1990), pp.86–93.
   "Production of Titanium Powders by the Calciothermic Reduction of TiO2" (in Japanese)
   K.Ono, T.H.Okabe, M.Ogawa and R.O.Suzuki

Chapter 1 in Part III

9. *Materials Transactions, JIM*, vol.31 no.1 (1990), pp.61–68.
   "Preparation of TiAl and Ti_3Al powders by Calciothermic Reduction of Oxides"
   R.O.Suzuki, M.Ikezawa, T.H.Okabe, T.Oishi and K.Ono
10. *Materials Transaction, JIM*, vol.32 no.3 (1991), pp.272–277.
    "Fundamental Study on Preparation of Al_3Ti Powders by Calciothermic Reduction of Oxides"
    R.O.Suzuki, T.Ueki, M.Ikezawa, T.H.Okabe, T.Oishi and K.Ono

Chapter 2 in Part III

11. To be published on *Metallurgical Transactions*, (submitted Dec. 1991, in press)
    "Deoxidation of Titanium Aluminide by Ca–Al Alloy under Controlled Aluminum Activity"
    T.H.Okabe, T.Oishi and K.Ono

12. To be published on *Proceedings of the 7th World Conference on Titanium*, San Diego June 28 – July 2 (1992)
    "Deoxidation of TiAl Intermetallic Compounds"
    T.H.Okabe, K.Fujiwara, T.Oishi and K.Ono

Chapter 3 in Part III

(Same as the papers in Chapter 1 in Part III)

Others

During the progress of this study, the author has published following papers and patents.

- *Metallurgical Transactions*, no.23B, August (1992) pp.415–421.
  "A Fundamental Study on the Preparation of Niobium Aluminide Powders by Calciothermic Reduction"
  T.H.Okabe, K.Fujiwara, T.Oishi and K.Ono

- *Boundary*, no.9 (1990) pp.10–13.
  "Extra–Low–Oxygen–Titanium which I produced" (in Japanese)
  T.H.Okabe:

- *Proceedings of the Conference on Electron Beam Melting and Refining*, Reno, Nov.(1989), pp.123–133.
  "Electron Beam Melting of Titanium and Quality Evaluation by Secondary Ion Mass Spectrometry"
  K.Ono, T.H.Okabe, N.Maeda and Y.Ueda:
- *Japanese Patent*, [H.2 14 March applied] (1990).
  "Production of Extra Low Oxygen Titanium" (in Japanese)
  T.Oishi, T.H.Okabe, M.Ikezawa, K.Ono and R.O.Suzuki:
- *Japanese Patent*, [H2. 15 March applied] (1990).
  "Production of Al_3Ti" (in Japanese)
  R.O.Suzuki, K.Ono, T.Oishi, T.H.Okabe, M.Ikezawa and T.Ueki
- *Japanese Patent*, [H.1 11 April applied] (1989).
  "Production of Ti_3Al" (in Japanese)
  R.O.Suzuki, K.Ono, T.Oishi, T.H.Okabe and M.Ikezawa

c. Awards

The author was awarded two prizes concerning this study.

- **15th Technological Development Prize**

  From the Japan Institute of Metals, at the 111th Fall Meeting of Japan Institute of Metals, Toyama, October 6 – 8 (1992).

  The awarded paper: *Journal of the Japan Institute of Metals*, vol.31 no.4 (1992) pp.315–317.
  "Production of Extra Low Oxygen Titanium by Calcium–Halide Flux Deoxidation"
  T.H.Okabe, M.Nakamura, T.Ueki, T.Oishi and K.Ono

- **3rd Prize on Student Poster Competition at the 7th World Conference on Titanium**

  From the Minerals, Metals and Materials Society (TMS, U.S.A), at the 7th World Conference on Titanium, San Diego, June 28 – July 2 (1992).

  The awarded paper: *Proceedings of the 7th World Conference on Titanium*, San Diego June 28 – July 2 (1992)
  "Deoxidation of TiAl Intermetallic Compounds"
  T.H.Okabe, K.Fujiwara, T.Oishi and K.Ono